Au/GaAs interface annealing study by positron-lifetime spectroscopy

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Structural changes of annealed Au contacts on semi-insulating GaAs have been observed by conventional positron lifetime-spectroscopy in which a significant fraction of positrons are drifted from a ^{22}Na source to the contact by an electric field. For annealing temperatures below $200\,^\circ$C it is found that the interface traps positrons into microvoids with a characteristic positron lifetime of 380 ± 10 ps. For annealing in the range of $300\,^\circ$C–$400\,^\circ$C a 150 ± 20 ps additional component appears in the lifetime spectra that is attributed to positrons annihilating from AuGa phases at the interface. The most likely explanation for this sudden onset of the positron component in the AuGa phases is that the changes in the GaAs near surface electron chemical potential, brought about by annealing, affect the interfacial dipole in such a way as to allow a favorable potential barrier for positron penetration into the metallic phase.

The Au/GaAs contact has been widely studied, having been subject to a variety of techniques such as Auger electron spectroscopy, Rutherford back scattering, and photoemission spectroscopy, but there still exist many uncertainties about the structure of the interface.[1] From these studies, however, a general picture has emerged of significant Ga and As chemical disolution into the Au overlayer even at room temperature.[2] Structural changes occur in the contact only when temperatures of around $200–250\,^\circ$C are reached, at which point significant As outdiffusion occurs leaving behind a Ga rich interfacial region.[3] At still higher temperatures ($>350\,^\circ$C) increased Ga and As outdiffusion and Au indiffusion is found to be accompanied by a precipitation of monocrystalline Au from AuGa phases.[4]

The present work is a development from the recent positron-lifetime study carried out on the nonannealed Au/GaAs semi-insulating (SI) system in our laboratory[5] and aims at demonstrating that conventional positron-lifetime spectroscopy can be used to study metal-semiconductor systems. In the previous work the Schottky-like junction was subjected to both forward and reverse bias. Moreover, the interface was found to contain many open-volume microvoids that trapped electric field drifted positrons and gave rise to a long lifetime component ($\sim$400 ps) in the lifetime spectra. In the forward bias condition the observed intensity of the microvoid component was found to be small, but with increasing reverse bias a large increase in the intensity was noted. This increase resulted from the deep donor $EL2$ ionization adjacent to the Schottky-like barrier causing an intense electric field to be experienced by positrons in its vicinity thus causing around 10% of positrons from the conventional ^{22}Na source to be drifted to the Au/GaAs (SI) interface. The fact that this was a large enough fraction for meaningful studies of the Au/GaAs interface to be carried out was a major motivation behind the present study.

The samples used in this study were obtained from ICI Wafer Technology Ltd. and were undoped liquid encapsulated Czochralski grown SI-GaAs(100) with a room temperature resistivity of 10^8 Ω cm and thickness 0.5 mm. The $EL2$ and C concentrations of the wafer were given as 1.5×10^{16} cm^{-3} and $9\pm6\times10^{14}$ cm^{-3}, respectively. Five identical sets of 10×10 mm^2 samples were prepared as previously detailed.[5] A 1000-Å Au layer was thermally evaporated onto the surfaces of each piece of the sample forming a circular spot of 8 mm diameter. The films were deposited by thermal evaporation from a W boat at a rate of 30–50 Å s^{-1} and in a vacuum of 1×10^{-6} Torr. Four of the identical sets of samples were annealed for 30 min at $100\,^\circ$C, $200\,^\circ$C, $300\,^\circ$C, and $400\,^\circ$C, respectively, while one set remained nonannealed. The annealing was performed under a flow of forming gas (80% N$_2$ and 20% H$_2$) to prevent oxidation.

The configuration of the samples and their electrical connections was essentially the same as that used previously.[5] As in our previous work a 25-μCi ^{22}Na source encapsulated in 1-μm-thick Ni foils was used in this work. A 100-V dc bias was then applied across the samples so that the internal electric field drifted positrons towards the injecting contacts. Positron-lifetime spectra were accumulated using a "fast-fast" coincidence spectrometer with a time resolution of 235 ps and approximately 2×10^6 counts were collected for each spectrum. Lifetime spectra were analyzed using the program POSITRONFIT,[6] great care being taken to correctly subtract the source corrections due to the Ni foils which exhibited a longer lifetime ($\sim$ 400 ps) similar in value to that coming from the Au/GaAs interface. For this procedure we first obtained a high count spectrum for nonmetalized SI-GaAs using a weak 1.5 μCi directly deposited source. Following Dannefaer *et al.*[7] this spectrum (3.5% of 404 ps and 96.5% of 223 ps) was taken as being free from source components. With the 1.5 μCi source removed and the 28 μCi Ni foil source inserted another high count spectrum was
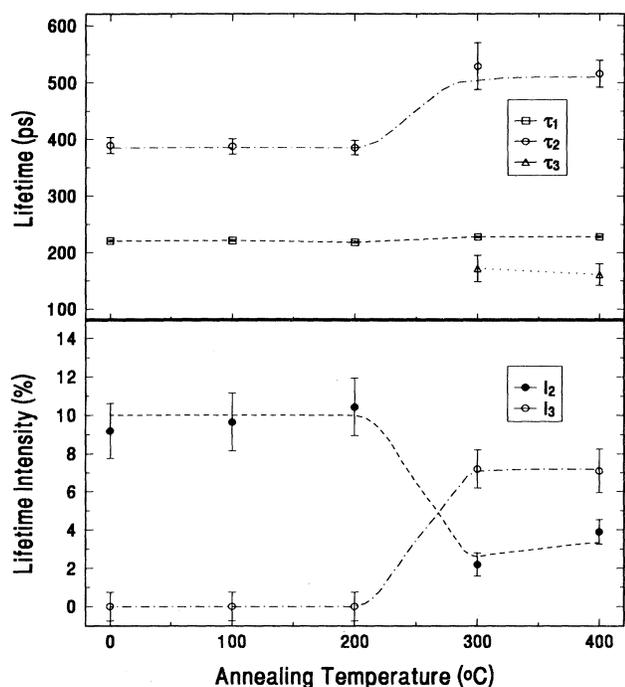
FIG. 1. Lifetimes and intensities of components in the lifetime spectra from Au/GaAs samples as a function of annealing temperature. The reverse bias applied to the Au/GaAs contacts is 100 V, with an estimated 6–7 % of positrons drifting to and annihilating from the interface.

FIG. 2. (a) Spatial structure of the interface employed in the present work. $j(t)$ is the positron current into the interface and f is the fraction of positrons that transmit into the Au-alloyed phases. (b) Schematic diagram of trapping from the substrate into interface microvoids. States $\mid b >$ and $\mid d >$ are those of positrons in the low electric field bulk and high field depletion regions, respectively (Ref. 5).

analyzed constraining the form of the SI-GaAs subspectrum, from which procedure a 15.5% Ni source spectrum was found. This spectrum, comprising 53% of 389 ps and 47% of 145 ps, was similar to the source correction (7.2% of a 390 ps) used by Dannefaer et al. for a 30-μCi Ni foil source.[7]

Figure 1 shows the experimental results of the lifetimes and their relative intensities as a function of annealing temperature. For the nonannealed, 100 °C and 200 °C annealed samples, two exponential components were found to fit the lifetime spectra well. The shorter component (τ_1), which corresponds to the GaAs bulk lifetime, is around 220–230 ps while the longer component (τ_2) of 380 ps is interpreted as that arising from positrons trapped in microvoids. The value of I_2 (10%) is consistent with the value obtained in Ref. 5 for a 100 V bias and does not change for these low temperature anneals.

The lifetime spectra corresponding to the annealing temperatures 300 °C and 400 °C could not obtain a good χ^2 value with a two component fit. However, by assuming three exponential components the lifetime spectra could be fitted well. As seen in Fig. 1 the microvoid lifetime τ_2 increases to about 500±20 ps and a shorter lifetime component τ_3 (150–185 ps) appears in the spectra, with the value of I_2 decreasing to about 3%.

With a nonfully microvoid trapping interface, a two-state model (semiconductor bulk and microvoid) is no longer suitable for samples annealed above 200 °C. Here, in a simple extension of our earlier work,[5] we construct a

three-state model (semiconductor bulk, microvoid, and Au-related alloy) to explain the measured results and estimate the interface microvoid concentration. This model is shown schematically in Fig. 2. The thermalized positron current $j(t)$ into the interface, being just determined by positron drift parameters in the semiconductor, remains identical to that used in the two-state model.[5] On reaching the interface, however, only a fraction (1-f) of positrons directly trap into microvoids. These microvoids are associated with the boundary between the single crystal substrate and the polycrystalline Au-related phases at the interface. They are most likely to be open volumes associated with grain boundaries. The trapping into these open-volume sites is most likely to be a two-state one, the first state being a weakly bound interface state with the positron delocalized in the plane of the interface boundary, followed by a trapping into a lower energy microvoid state the latter being localized somewhere along the boundary. This process is analogous to that of dislocation trapping at low temperatures in which the positron subsequently traps into a vacancy.[8] The remaining fraction f of drifted positrons lose little or no energy at the boundary and penetrate directly into Au or Au-related microcrystals. The fact that positrons are able to transit from GaAs to such microcrystals is not unexpected since one prediction gives the energy barrier for positrons at the Au/GaAs interface as < 0.14 eV.[5] Once in the Au-related phases they annihilate at a faster rate λ_3 but are also subject to trapping into microvoids

with trapping rate given by[8]

$$\kappa = 4\pi R D_+ C_v \qquad (1)$$

where R is the radius of the microvoid, D_+ is the diffusion coefficient for positrons in the microcrystal, and C_v is the microvoid concentration. Considering a single microvoid state, which has the two population mechanisms mentioned and taking the detrapping of positrons from microvoids to be negligible, the following rate equations describe the system:

$$\frac{dn_2(t)}{dt} = -\lambda_2 n_2 + \kappa n_3 + (1-f)j(t) \ ,$$
$$\frac{dn_3(t)}{dt} = -\lambda_3 n_3 - \kappa n_3 + f j(t) \ , \qquad (2)$$

where

$$j(t) = \begin{cases} N\alpha v_d e^{-(\alpha v_d + \lambda_b)t} & (t < W/v_d) \\ N\alpha v_b e^{-\lambda_b t} e^{-\alpha[v_b t + (1 - v_b/v_d)W]} & (t \geq W/v_d) \end{cases}$$
$$(3)$$

and where n_2 and n_3 correspond to the numbers of positrons in the microvoid and interface Au-related alloy structures, respectively. Here W is the depletion region width, α^{-1} is the mean positron implantation depth, and v_b and v_d are the positron drift velocities in the bulk and depletion regions of the substrate, respectively. Similarly λ_b and λ_2 are the bulk and microvoid annihilation rates, respectively.

From Eqs. (2) and (3) the relative intensities of positrons annihilating in interfacial microvoids I_2 and Au-related alloy I_3 under the conditions $v_b \ll v_d < \lambda_b/\alpha$ may be shown to be[9]

$$I_2 = \frac{\alpha v_d[\kappa + (1-f)(\lambda_3 - \lambda_2)][1 - e^{\alpha W(1 + \lambda_b/\alpha v_d)}]}{(\alpha v_d + \lambda_b - \lambda_2)(\lambda_3 + \kappa - \lambda_2)} \qquad (4)$$
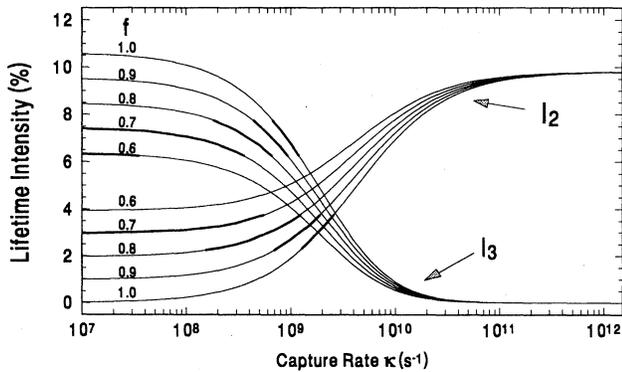
FIG. 3. Model prediction for the lifetime intensity components of the two Au/GaAs interface states as a function of microvoid trapping rate κ. I_2 is the component deriving from microvoids and I_3 is that from Au-alloyed phases. The highlighted portions indicate the experimentally observed values of I_2 and I_3 after annealing at 300 and 400 °C.

and

$$I_3 = \frac{f\alpha v_d(\lambda_3 - \lambda_2)[1 - e^{-\alpha W(1 + \lambda_b/\alpha v_d)}]}{(\alpha v_d + \lambda_b - \lambda_3 - \kappa)(\lambda_3 + \kappa - \lambda_2)} \ . \qquad (5)$$

As expected, Eq. (4) reduces to Eq. (12) of Ref. 5 under the conditions $f = 0$ (complete trapping into metal-semiconductor boundary microvoids) and $\kappa \to \infty$ (saturation trapping by Au overlayer microvoids). These cases, which are experimentally indistinguishable, are representative of the nonannealed, 100 °C and 200 °C samples since we have not been able to resolve any short Au-related lifetime component in these spectra.

In the case of the 300 °C and 400 °C annealed samples the indistinguishability between these two types of microvoid trapping processes is not present. This may be seen from Fig. 3 which shows the dependence of the lifetime intensities I_2 and I_3 on the trapping rate κ for different values of f. The highlighted parts of the curves show, inclusive of a 1σ error bar, the experimentally observed values of I_2 and I_3. It is noted that a high value of $f = 1$ is not allowed since there is no value of κ capable of giving both I_2 and I_3. Moreover, low values of $f \leq 0.6$ are also forbidden since these would not give sufficient positrons entering the Au-alloyed phases to explain the observed value of I_3. An acceptable range of f is seen to be between 0.6 and 0.8. It is also noted that the trapping rate κ must be less than 3×10^8 s^{-1}. From this observation we may use Eq. (1) to put a limit on the concentration of microvoids in the 300 °C and 400 °C annealed samples. Since it known that D_+ values for most metals lie in the range 0.04–1 cm^2 s^{-1}(Ref. 10) and from the value of τ_2 that the mean radius R of the microvoids is 7 Å (Ref. 5) we find the concentration of microvoids in these higher temperature annealed samples to be less than 5×10^{15} cm^{-3}.

With reference to the sharp transition occurring between 200 and 300 °C it might be argued that interdiffused Au could dope the GaAs in such a way as to reduce the near contact electric field in the higher temperature range. Such arguments would however seem untenable on a number of grounds. In the first place it is known that there is no sudden increase in Au indiffusion in this temperature range. Rather the Au diffuses into the GaAs to depths of 0.15–1 μm in as-deposited films even at room temperature with a penetration that does not increase significantly beyond this until temperatures in excess of 400 °C are reached.[11,12] While there is currently some uncertainty about the question of acceptor and donor states induced by Au diffusion in GaAs (Refs. 13, 14, and 3), we point out that penetration of any metalicity into the substrate is unlikely to alter the spatial electric field structure seen by positrons significantly. If, as seems to be the case, that the Au induces shallow acceptors[13] the metallic part of the interface will penetrate into the GaAs and the electric field profile will shift laterally by the penetration depth. Such a shift (~ 1 μm), apart from being expected to the same extent at all annealing temperatures, would not affect the positron diffusion significantly as positrons are implanted over much larger distances (~ 50 μm).

The annealing-induced drop in I_2 could also be ex-

plained if the concentration of interface microvoids were to undergo a sudden lowering so that not all the positrons drifting to the interface are subject to saturation trapping into microvoids. On such interpretation for the nonannealed 100 °C and 200 °C samples, the concentration of microvoid type defects at the interface would be so large that essentially all the positrons drifting from the bulk region are trapped into these defects. Moreover, the increase in τ_2 from 380 ps to 500 ps for annealing above 200 °C could be explained by an increase in average microvoid diameter from ~ 6 Å to ≥ 13 Å,[15] as the original microvoids migrate and coalesce to form larger voids. While such an interpretation cannot easily be disproved, it does suggest too large a concentration of microvoid defects in the as-grown film, if as expected these defects are associated with grain boundaries. As seen from Fig. 3, for I_3 to be nondetectable, capture rates greater than 5×10^{10} s^{-1} are required. This in turn, taking reasonable values of microvoid radius and D_+ in Eq. (1), suggests microvoid concentrations in excess of $10^{17}/10^{18}$ cm^{-3} and mean microvoid separations between 100 and 300 Å. Such values are difficult to accomodate with the known grain size ~ 500 Å for films grown under similar evaporation rates.[4]

Here it is suggested that a more likely explanation for the sudden onset of the short component at 300 °C and above is to be found by correlating this observation with the known near surface Fermi energy positions as obtained from photoemission spectroscopy and I-V and C-V measurements.[14] These studies indicate a sharp rise in the Fermi energy pinning position (~ 0.2 eV) in the same temperature range 200–300 °C. Whatever its cause, such a change in Fermi energy will decrease the positron affinity[17] for the semiconductor making it more energetically favorable for the positron to transit to the Au overlayer. This fact results from the interface dipole depending on not just the electron chemical potentials in semiconductor and metal, but also on the Fermi level positioning relative to the valence band [cf. Eq. (19) of Ref. 5]. As pointed out by Shan et al.[5] the effective energy barrier seen by a positron approaching the Au/GaAs interface from the semiconductor side is expected to be very small (≤ 0.14 eV), and with the mentioned decrease in effective GaAs positron affinity this barrier would become negative with the interface allowing positrons to transmit to the Au region. In this picture the smaller microvoids in the interface would present a smaller capture cross section after the interface becomes transmitting and the mean sample microvoid would have larger radius and longer characteristic lifetime thus explaining the observed increase in τ_2.

In the work of Newman et al.[14] two mechanisms both involving Au-induced defects in the near surface GaAs lattice have been invoked to explain the shift of the Fermi energy on the semiconductor side.[14] The first of these involves consideration of induced deep acceptor and donor state at energies below the conduction band minimum of 0.7 and 0.95 eV, respectively, while the second involves only the 0.7 eV deep acceptor and in addition the Au_{Ga} defect. In the present work these two models cannot be distinguished since both give rise to the same change in the Fermi energy position, the result of which is an interface dipole more favorable to the passage of positrons into the metallic film. However, in the first of the two models where pinning reverts to the acceptor level as a result of less electron affinic Au_2Ga precipitates[4] replacing the most strongly electron affinic Au, it is likely that the positron chemical potential of the metallic film also increases in magnitude as Au is replaced by the AuGa phase, making transmission through the interface even more favorable. Although positron chemical potentials have not yet been calculated for Au_2Ga or Ga rich Au, the work of Puska et al.[17] suggests that the positron chemical potential for Au (-1.86 eV) is considerably higher than typical elements in the region of Ga (Al, Si, and Ge) thus lending support to this view.

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