Mutual Passivation of Group IV Donors and Nitrogen in Diluted GaN_xAs_{1-x} Alloys

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ABSTRACT

We demonstrate the mutual passivation phenomenon of Ge donors and isovalent N in the highly mismatched alloy GaN_xAs_{1-x} doped with Ge. Layers of this alloy were formed by the sequential implantation of Ge and N ions followed by pulsed laser melting and rapid thermal annealing. The mutual passivation effect results in the electrical deactivation of Ge_{Ga} donors (Ge on Ga sites) and suppression of the N_{As} (N on As sites) induced band gap narrowing through the formation of Ge_{Ga}-N_{As} nearest neighbor pairs. These results in combination with the analogous effect observed in Si-doped GaN_xAs_{1-x} provide clear evidence for the general nature of the mutual passivation phenomenon in highly mismatched semiconductor alloys.

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GaN_xAs_{1-x} (with x typically less than 0.05) belongs to the class of highly mismatched semiconductor alloys (HMAs) in which small quantities of more electronegative elements (N) replacing the metallic anions (As) cause dramatic changes in the alloy's electronic properties.[1-5] The unusual properties of HMAs have been successfully described by the anticrossing interaction between localized states of the foreign electronegative element (N) and the extended states of the host semiconductor matrix.[1,6] Such interaction gives rise to a drastic reduction of the band gap, a large increase in the electron effective mass,[7,8] and an increase in the density of states of the conduction band.[7] As a consequence, over an order of magnitude enhancement in the maximum achievable free electron concentration has been demonstrated in GaN_xAs_{1-x} thin films doped with group VI donors (Se and S).[9-11] However, doping the material with Si resulted in a highly resistive GaN_xAs_{1-x} layer.[12]

Our recent investigation of epitaxially grown GaN_xAs_{1-x} thin films doped heavily with Si revealed that the Si and N mutually passivate each other's electronic activity.[13] The reduced electrical activity of Si_{Ga} donors (Si on Ga sites) in GaN_xAs_{1-x} alloys was attributed to the formation of nearest neighbor Si_{Ga}-N_{As} pairs. Since isovalent nitrogen (N_{As}) is responsible for a massive modification of the electronic structure of GaN_xAs_{1-x} alloys, the formation of these Si_{Ga}-N_{As} pairs affects the conduction band structure by deactivating a fraction of the N_{As} sites. In this paper we use Ge doping of GaN_xAs_{1-x} to demonstrate that the mutual passivation effect is a general phenomenon applicable to all group IV donors in the highly mismatched alloy GaN_xAs_{1-x}.

The Ge doped GaN_xAs_{1-x} layers were synthesized by sequential implantation of Ge and N ions into GaAs followed by a combination of pulsed laser melting (PLM) and rapid thermal annealing (RTA). 340 and 100 keV Ge ions were implanted into semi-insulating GaAs substrates with doses of $6.4\text{x}10^{15}$ and $1.7\text{x}10^{15}\text{cm}^{-2}$, respectively. Matching N distributions were obtained by dual energy N^+-implantation of 80 and 33keV with doses of $7.0\text{x}10^{15}$ and $2.4\text{x}10^{15}$ cm^{-2}, respectively. This Ge^+ and N^+ co-implantation created a ~200nm thick layer of Ge and N co-doped GaAs with ~2 mole percent (~4.4×10^{20}cm^{-3}) of both species (2%N+2%Ge). Layers produced from only N (2%N) or Ge (2%Ge) ion implantation were also used as references. The implanted GaAs samples were subjected to PLM in air using a KrF laser (λ= 248 nm) with a FWHM pulse duration of ~38ns and fluence of 0.45 J/cm^2. The samples were subsequently processed by RTA at temperatures between 600 and 950°C for 5-120 seconds in flowing N_2. This post-implantation pulsed laser melting and rapid thermal annealing approach will be referred to as PLM-RTA. We have recently utilized this method to realize GaN_xAs_{1-x} layers with x as high as 0.016.[14,15]

The free carrier concentration was measured by the Hall Effect technique in the Van de Pauw geometry. Electrochemical capacitance-voltage measurements (ECV) were also carried out to determine the net dopant concentration profiles. The band gaps of the films were measured using photomodulated reflectance (PR) at room temperature using a chopped HeCd laser beam (λ=442 nm or 325nm) for modulation. The spectral line widths and band gaps were determined by fitting the PR spectra to the Aspnes third-derivative functional form.[16]

The passivation of the N activity by the Ge atoms in the 2%N+2%Ge sample after PLM-RTA is illustrated in the series of photoreflectance (PR) spectra presented in Fig. 1. A fundamental band gap transition at 1.24 eV is observed for GaAs samples implanted with 2% N alone after PLM-RTA at 950ºC for 10-120 s, corresponding to ~1 mole percent incorporation of N in the substitutional As sites (N_{As}). In contrast, the band gap of the 2%N+2%Ge samples increases from 1.24 to 1.42 eV (band gap of GaAs) as the RTA duration increases to 60s, revealing that N_{As} is passivated by Ge. We propose that the sufficiently short melt duration (~200 ns) during PLM leads to the incorporation of the Ge and N atoms to levels far beyond equilibrium randomly in their preferential sublattice. During subsequent RTA, the temperature is sufficient to enable Ge atoms to diffuse to attain a lower-energy configuration. Since N is more electronegative than As

(Pauling electronegativities of N and As are 3.0 and 2.0, respectively) it has a tendency to bind the fourth valence electron of Ge atoms in Ga sites Ge_{Ga}, and therefore the formation of Ge_{Ga}-N_{As} nearest-neighbor pairs is favored energetically. The gradual increase in the band gap of the 2%N+2%Ge sample as a function of RTA temperature and/or time duration can therefore be attributed to the passivation of N_{As} by Ge_{Ga} through the formation of nearest neighbor Ge_{Ga}-N_{As} pairs. The estimated diffusion length of Ge in GaAs at 950°C for 10s is ~2-20 Å (due to the uncertainties in the diffusion coefficient of Ge)[17]. This is comparable to the average distance from a Ge atom to its nearest N_{As} for GaN_xAs_{1-x} with x~0.01 (~10.3Å).

The change in the band gap of the GaAs samples containing both N and Ge together and N alone and processed identically is shown as a function of RTA duration in the inset of Fig. 1. Results from another set of samples implanted with 4%N+2%Ge and 4%N alone are also shown. For the sample implanted with 4% N, GaN_xAs_{1-x} is formed with a band gap of 1.17 eV, which corresponds to x=0.016. After PLM-RTA at 950ºC for 10 s, the band gap of the 4%N+2%Ge sample (1.36 eV) becomes closer to that of GaAs compared to the band gap of the 2%N+2%Ge sample (1.29 eV). Such observation shows that the passivation process is controlled by the diffusion of randomly distributed Ge atoms to a Ga site with a N_{As} nearest neighbor. The average distances from a Ge atom to its nearest N_{As} are ~10.3 and 8.8 Å for the 2% (x=0.01) and 4% N (x=0.016) implanted samples, respectively. Therefore for a given amount of Ge in GaN_xAs_{1-x} (with Ge concentration higher than x) and the same annealing conditions, a larger fraction of N_{As} is passivated by Ge_{Ga} for samples with higher x.

Since N_{As} has a tendency to bind the fourth valence electron of Ge_{Ga} donors, we expect a reduction of the concentration of electrically active Ge donors. Figure 2 shows a comparison of the electron concentration of the 2%N+2%Ge and 2%Ge samples followed by PLM-RTA for 10s in the temperature range of 650 to 950°C. For both samples the electron concentration approaches $10^{19}cm^{-3}$ after PLM. Experimentally, the maximum free electron concentration n_{max} in GaAs achievable under equilibrium growth conditions is limited to the mid 10^{18}cm^{-3} range, corresponding to the Fermi energy E_F located approximately at 0.1 eV above the conduction band edge.[18,19] The electron concentration exceeding the equilibrium n_{max} results from the highly non-equilibrium rapid melting and solidification in the PLM process.

For the 2%Ge sample, thermal annealing after PLM drives the system toward equilibrium with an electron concentration of ~1x10^{18}cm^{-3}. This electron concentration is consistent with the amphoteric nature of Ge in GaAs.[20,21] The electron concentration of the 2%N+2%Ge samples, on the other hand, drops over two orders of magnitude to lower than 10^{17}cm^{-3} as the samples are subjected to RTA at temperatures higher than 650ºC. This is consistent with the passivation of Ge_{Ga} donors via the formation of N_{As}-Ge_{Ga} pairs by Ge diffusion during RTA, similarly to the case in Si doped GaN_xAs_{1-x}.[13]

It has been widely recognized that the N-induced modifications of the conduction band lead to a drastic reduction of the electron mobility in GaN_xAs_{1-x}, typically ranges from ~10 to a few hundred cm^2/Vs.[9,22] During the post-implantation treatment, it is expected that some of the Ge diffused out of the N-implanted region forming a layer of Ge doped GaAs below the GaNAs:Ge layer. Hall effect measurements may be complicated when such parallel layers with very different electrical behaviors co-exist in the sample.[10,23] The electrical behavior of the GaN_xAs_{1-x}:Ge samples are therefore further studied by ECV profiling.

Figure 3 shows three ECV profiles for the 2%Ge sample PLM-RTA at 950ºC for 10 s and the 2%N+2%Ge samples PLM-RTA at 950ºC for 10 s and 60 s. The Ge and N atomic distributions calculated using the PROFILE code[24] are also shown in the figure for comparison. PLM-RTA at 950ºC for 10 s leads to a strong decrease in the donor concentration for the 2%N+2%Ge sample as compared to the 2%Ge alone sample, consistent with the Hall effect measurements.

A striking effect is observed in the 2%N+2%Ge sample after RTA at 950ºC for 60 s. In this case the top ~0.25 μm layer is p-type, followed by an n-type layer below. The p-n junction depth in this sample corresponds to the melt depth in GaAs for PLM using a fluence of 0.45 J/cm^2.[15] The p-type activity in the top layer in this sample is attributed to the complete passivation of Ge_{Ga} by N_{As} through the formation of Ge_{Ga}-N_{As} nearest neighbor pairs in the laser melted region. The electrical activity of the small concentration of Ge_{As} acceptors is revealed once the Ge_{Ga} donors are passivated by N_{As} in the PLM region. In Fig.1 notice that PR measurements on this sample show a band gap similar to that of GaAs, suggesting that the ~2x10^{20}cm^{-3} of N atoms are passivated by Ge atoms. We also note that GaNAs:Si samples formed by co-implantation of Si and N processed by PLM- RTA were highly resistive with no p-n junction formed. This is consistent with less amphoteric nature of Si compared to Ge in GaAs.

In conclusion, a comparison of the band gap and the electrical behavior in the GaAs samples implanted with Ge alone and N+Ge followed by PLM-RTA shows that the formation of Ge_{Ga}-N_{As} pairs results in a *mutual passivation* of both species: it eliminates the electrical activity of Ge_{Ga} donors and deactivates N_{As} as the isovalent dopant. Consequently, Ge doping in GaN_xAs_{1-x} under equilibrium conditions results in a highly resistive or p-type GaN_xAs_{1-x} layer with the fundamental band gap governed by a net "active" N, roughly equal to the total N content minus the Ge concentration. These results together with our previous report on the mutual passivation of Si and N in GaN_xAs_{1-x} clearly demonstrate a general nature of this phenomenon. Moreover, the ability to use PLM for a spatially controlled passivation provides a unique opportunity for the fabrication of novel planar and three-dimensional structures by the selective implantation of either one or both species. The mutual passivation effect described here may therefore be exploited for electrical isolation, band gap engineering, and quantum confinement.

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FIGURE CAPTIONS

Fig. 1 Photomodulated reflectance (PR) spectra measured from a series of GaAs samples implanted with 2%N+2%Ge followed by PLM-RTA at 950ºC for a duration of 5-120 s. PR spectra from a GaAs wafer (top spectrum) and a GaAs sample implanted with 2%N only after PLM+RTA at 950ºC for 120 s. (bottom spectrum) are also shown. The inset shows the band gap energies determined from the PR measurements from 2%N, 2%N+2%Ge, 4%N and 4%N+2%Ge samples after PLM+RTA at 950ºC for durations of 5-120 s.

Fig. 2 Free electron concentrations of the 2%Ge and 2%N+2%Ge samples after PLM+RTA at increasing temperature for 10 s. obtained by Hall effect measurements. Electron concentration for the 2%N+2%Ge sample after PLM+RTA at 950ºC for 60 s is also shown.

Fig. 3 Net donor (acceptor) concentration profiles obtained by electrochemical capacitance-voltage (ECV) measurements for a GaAs sample implanted with 2%Ge followed by PLM-RTA at 950ºC for 10 s and GaAs samples implanted with 2%N+2%Ge processed by PLM-RTA at 950ºC for 10 s and 60 s. The calculated Ge and N atomic distributions are also shown in the figure for comparison.

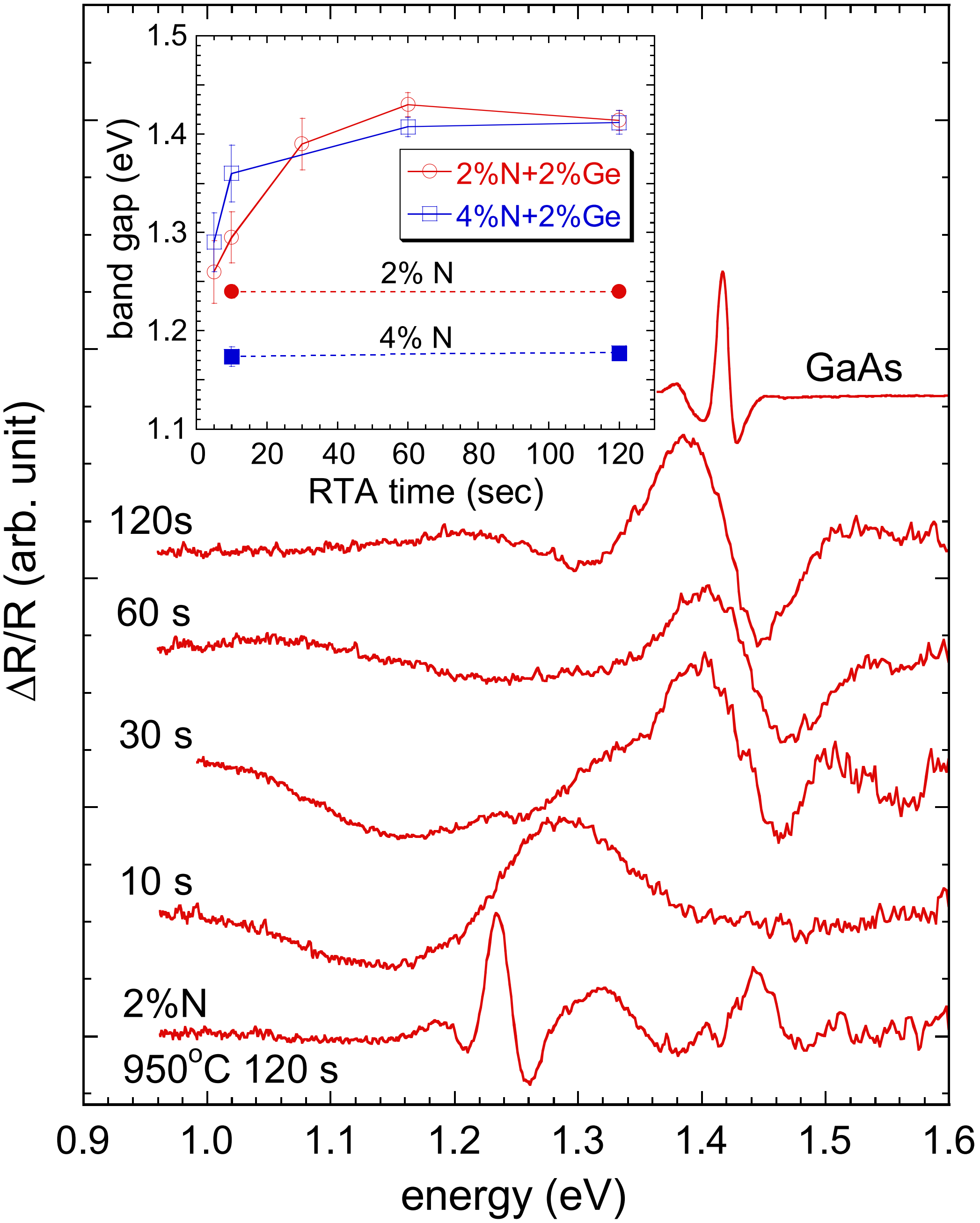
ΔR/R (arb. unit)
energy (eV)
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
GaAs
120s
60 s
30 s
10 s
2%N
950°C 120 s
band gap (eV)
RTA time (sec)
1.1
1.2
1.3
1.4
1.5
0
20
40
60
80
100
120
2%N+2%Ge
4%N+2%Ge
2% N
4% N

Figure 1

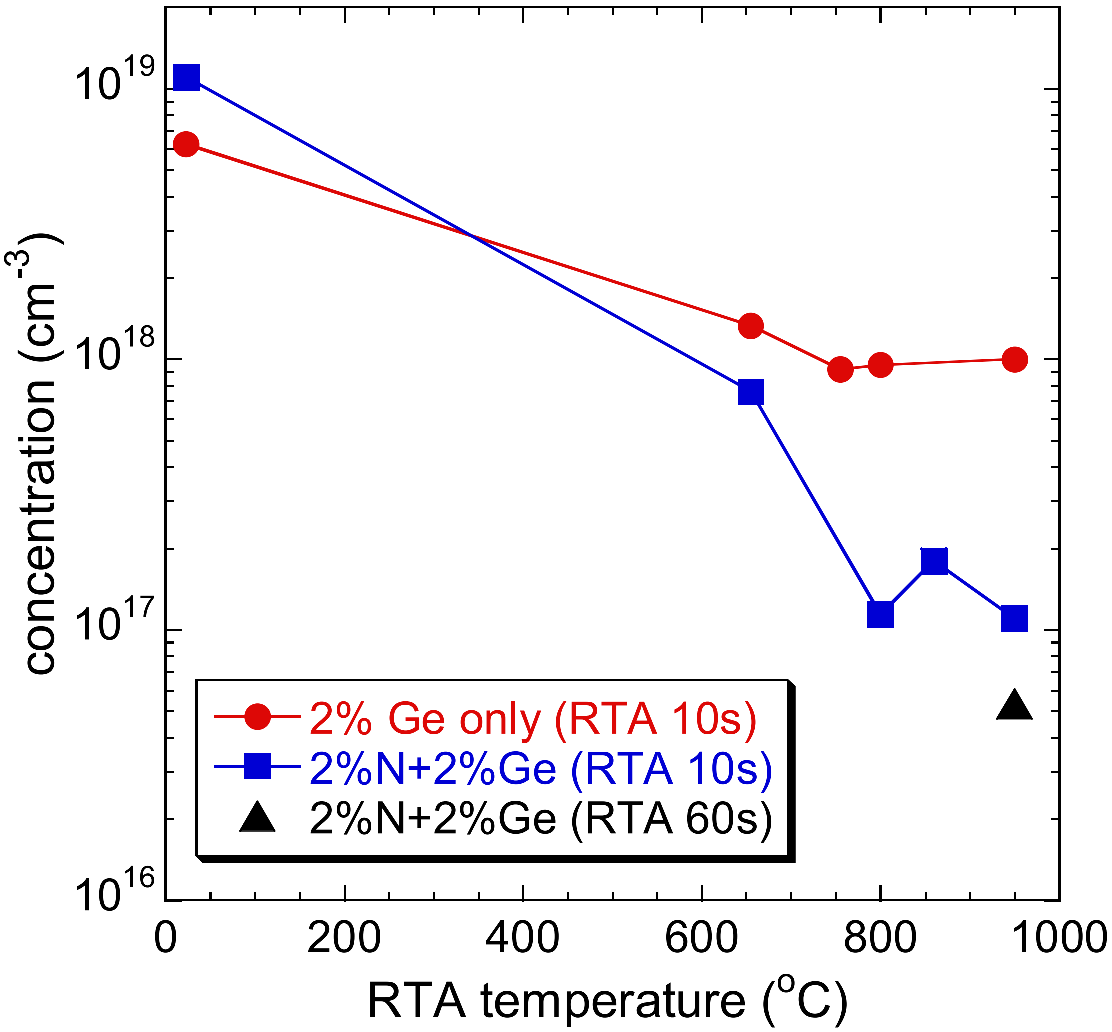
concentration (cm^{-3})
10^{19}
10^{18}
10^{17}
10^{16}
0
200
400
600
800
1000
RTA temperature (^{o}C)
2% Ge only (RTA 10s)
2%N+2%Ge (RTA 10s)
2%N+2%Ge (RTA 60s)

Figure 2

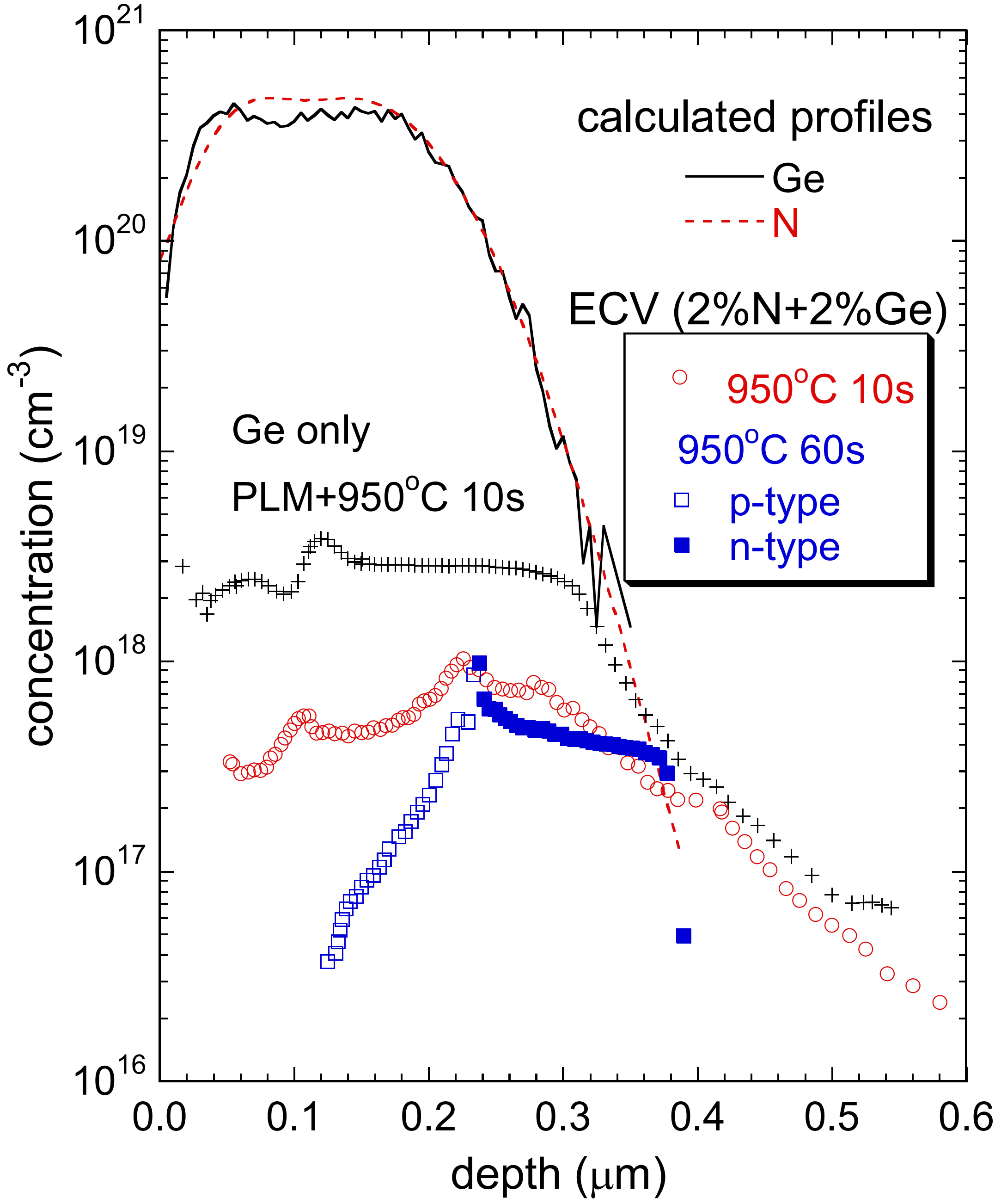
calculated profiles
Ge
N
ECV (2%N+2%Ge)
950°C 10s
950°C 60s
p-type
n-type
Ge only
PLM+950°C 10s
concentration (cm^{-3})
depth (μm)
10^{21}
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
0.0
0.1
0.2
0.3
0.4
0.5
0.6

Figure 3