Mutual passivation of group IV donors and isovalent nitrogen in diluted $GaN_xAs_{1-x}$ alloys

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We demonstrate the mutual passivation of electrically active group IV donors and isovalent N atoms in the $GaN_xAs_{1-x}$ alloy system. This phenomenon occurs through the formation of a donor-nitrogen bond in the nearest neighbor $IV_{Ga}$-$N_{As}$ pairs. In Si doped $GaInN_{0.017}As_{0.983}$ the electron concentration starts to decrease rapidly at an annealing temperature of 700ºC from ~$3x10^{19}cm^{-3}$ in the as-grown state to less than $10^{16}cm^{-3}$ after an annealing at 900ºC for 10 s. At the same time annealing of this sample at 950ºC increases the gap by about 35 meV, corresponding to a reduction of the concentration of the active N atoms by an amount very close to the total Si concentration. We also show that the formation of $Si_{Ga}$-$N_{As}$ pairs is controlled by the diffusion of Si via Ga vacancies to the nearest $N_{As}$ site. The general nature of this mutual passivation effect is confirmed by our study of Ge doped $GaN_xAs_{1-x}$ layers formed by N and Ge co-implantation in GaAs followed by pulsed laser melting.

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The $GaN_xAs_{1-x}$ alloys (with x up to 0.05) have exhibited many unusual properties as compared to the conventional binary and ternary semiconductor alloys [1-4]. For example, a strong band gap reduction by as much as 180 meV per mole percent of N (i.e. for $x$=0.01) has been observed [1]. These unusual properties have been successfully described by an anticrossing interaction between localized states of the N and the extended states of the GaAs matrix that splits the conduction band into two subbands [5-7]. Another manifestation of the band anticrossing (BAC) is a considerable flattening of the dispersion relation for the lower subband near its minimum leading to a large increase of the electron effective mass [7].

As a result of the N-induced conduction band modifications in $GaN_xAs_{1-x}$ an enhancement of the maximum achievable free electron concentration $n_{max}$ has been predicted [8]. In a heavily Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ thin film with $x$~0.033, $n_{max}$ as high as $7x10^{19}cm^{-3}$ was achieved, more than an order of magnitude larger than that of GaAs [8-10]. However, doping $GaN_xAs_{1-x}$ with group IV donors (Si) results in highly resistive material [11]. In this paper we show that the striking asymmetry in the behavior of group VI and IV donors can be explained by an entirely new effect in which an electrically active substitutional group IV donor and an isoelectronic N atom passivate each other's electronic effects [12]. This mutual passivation occurs in $GaN_xAs_{1-x}$ doped with group IV donors (Si and Ge) through the formation of nearest neighbor $IV_{Ga}$-$N_{As}$ pairs.

The band gap of the films was measured using photomodulated reflectance (PR) at room temperature using a 300W halogen tungsten lamp dispersed by a 0.5m monochromator as a probe beam. A chopped HeCd laser beam ($\lambda$=442 nm) provided the photomodulation. The free carrier concentration and mobility in the samples were measured by the Hall effect technique in the Van de Pauw geometry.

Fig. 1 shows the free electron concentration on MBE-grown Si doped $Ga_{0.93}In_{0.07}N_{0.017}As_{0.983}$ and GaAs and a MOCVD-grown Se doped $Ga_{0.92}In_{0.08}N_{0.024}As_{0.976}$ thin films after RTA for 10 sec in the temperature range of 650-950ºC. In is added to the GaNAs alloy to compensate for the strain due to the presence of N and does not play an important role to the effects discussed here. The Si and Se doping levels in these samples are in the range of $2\text{-}9\times10^{19}$cm$^{-3}$ and ~$2\times10^{20}$cm$^{-3}$, respectively. For both the GaAs:Si and GaInNAs:Se samples, as the RTA temperature increases we observe only slight decreases in electron concentrations, from $1.6\times10^{19}$ to $8\times10^{18}$cm$^{-3}$ for GaAs:Si and $3\times10^{19}$ to $2\times10^{19}$cm$^{-3}$ for GaInNAs:Se. Such a decrease in the electron concentration in GaAs is in agreement with the equilibrium maximum electron concentration (in the range of $10^{18}$-$10^{19}$cm$^{-3}$) suggested by the amphoteric native defect model [13]. The much higher electron concentration in the Se doped GaInNAs sample is also consistent with the modified conduction band structure due to N incorporation in the alloy [8].

In striking contrast, the free electron concentration in the GaInNAs:Si sample drops from $1.1\times10^{19}$cm$^{-3}$ in the as-grown film to $3\times10^{17}$cm$^{-3}$ after RTA at 950ºC for 10 s In fact, RTA at 950ºC for 120 s further reduces the electron concentration to $<10^{15}$cm$^{-3}$. The reduced electrical activity of Si donors in $GaN_xAs_{1-x}$ alloys can be attributed to the formation of nearest neighbor $Si_{Ga}$-$N_{As}$ pairs. The highly electronegative N atom strongly binds the fourth valence electron of Si, preventing it from acting as a hydrogenic donor.

Such an explanation suggests that because of the localized nature of the N-states in $GaN_xAs_{1-x}$ the passivation is limited to group IV donors that occupy Ga sites. This is supported by the small change in electrical behavior observed in the GaInNAs:Se thin film in which both the N and Se reside in the As sublattice and therefore cannot form nearest neighbor passivating pairs.

The well-defined onset temperature of about 700ºC for the observed reduction of electron concentration in GaInNAs:Si shown in Fig. 1 roughly corresponds to the annealing condition that allows the Si atoms to diffuse over a length equal to the average distance between randomly distributed Si and N atoms (~ 7Å) [12]. The diffusion-passivation process is analyzed in the context of Si diffusion mediated by both neutral Ga vacancies ($V_{Ga}^{0}$) and triply negatively charged Ga vacancies ($V_{Ga}^{3-}$) [14]. Figures 2 shows the isothermal annealing effects of the free carrier concentration of the GaInNAs:Si sample for annealing temperature in the range of 650-820ºC. Calculations based on Si diffusion via Ga vacancies are shown as dashed lines in Figures 2. The calculations based on Si diffusion via $V_{Ga}^{0}$ and $V_{Ga}^{3-}$ agree very well with the experimental data. According to the diffusion model, at high annealing temperatures or long annealing time, the Fermi-level independent, $V_{Ga}^{0}$-mediated diffusion becomes increasingly important. This is reflected in the fact that the $\ln[n/n_0] \sim t$ curves approach a linear dependence at high temperatures or long anneal times [14].

Since isovalent N is responsible for a massive modification of the electronic structure of $GaN_xAs_{1-x}$ alloys [6,7] the question arises to what extent the formation of these pairs affects the effects of N atoms in the alloys. Photoreflectance measurements on the GaInNAs:Si sample show that the band gap energy increases with increasing RTA temperature. Annealing of the sample at 950ºC increases the gap by about 35 meV. If this increase is attributed to deactivation of the N atoms the concentration of the deactivated N is approximately equal to $0.004\times2.2\times10^{22}cm^{-3} \sim 8\times10^{19}cm^{-3}$, which is close to the initial total Si concentration in the as-grown sample. This is consistent with the formation of $Si_{Ga}$-$N_{As}$ pairs being responsible for the mutual passivation of both species. This scenario of the passivation process is further corroborated by photoluminescence (PL) measurements on the GaInNAs:Si sample. A strong PL peak at ~0.8eV is observed when the sample is mutually passivated, indicating the presence of deep states associated with the $Si_{Ga}$-$N_{As}$ pairs [12].

The general nature of the mutual passivation effect is supported by investigations of $GaN_xAs_{1-x}$ layers doped with Ge, another group IV donor. 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) [15]. PLM was carried out using a KrF laser (λ= 248 nm) with pulse duration~38ns and fluence of 0.45 J/cm$^2$. We have recently utilized this (PLM-RTA) method to realize $GaN_xAs_{1-x}$ layers with x as high as 0.016 [16]. Sequential multi-energy $Ge^+$ and $N^+$-implantation were used to create a ~200nm thick layer of Ge and N co-doped GaAs with ~2 mole percent (~$4.4\text{x}10^{20}cm^{-3}$) of both species (2%N+2%Ge). Layers implanted with N (2%N) or Ge (2%Ge) only and subjected to the sample PLM and RTA treatments implantation were used as references.

The passivation of the N activity by the Ge atoms is illustrated in the series of PR spectra presented in Fig. 3. The band gap energies obtained from the PR spectra are shown in the inset as a function of the duration of 950ºC RTA treament. 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 a $GaN_xAs_{1-x}$ layer with x~0.01. In contrast, the band gap of the 2%N+2%Ge samples after PLM increases from 1.24 to 1.42 eV (band gap of GaAs) as the RTA duration increases to 60s, revealing that all $N_{As}$ sites are passivated by Ge. 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 be attributed to the passivation of $N_{As}$ by $Ge_{Ga}$ through the formation of nearest neighbor $Ge_{Ga}$-$N_{As}$ pairs.

Fig. 4 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. The electron concentration of both samples approaches $10^{19}cm^{-3}$ after PLM. For the 2%Ge sample, thermal annealing after PLM drives the system toward equilibrium with an electron concentration of ~$1x10^{18}cm^{-3}$ which is consistent with the amphoteric nature of Ge in GaAs [17]. The electron concentration of the 2%N+2%Ge samples, on the other hand, drops over two orders of magnitude to less than $10^{17}cm^{-3}$ as the samples are subjected to RTA at temperatures higher than 650ºC. The changes in the band gap and the electrical behavior in the Ge doped $GaN_xAs_{1-x}$ sample show that the activities of Ge donors and isovalent N mutually passivate each other via the formation of $N_{As}$-$Ge_{Ga}$ pairs,, just as was the case in Si doped $GaN_xAs_{1-x}$.

In conclusion, we have studied the mutual passivation phenomenon observed in $Ga_{1-y}N_xAs_{1-x}$ alloys doped with group IV donors. It is shown that upon thermal annealing, both Si and Ge donors diffuse in the Ga sublattice until forming $Si_{Ga}$-$N_{As}$ and $Ge_{Ga}$-$N_{As}$ nearest-neighbor pairs. This process results in the mutual passivation of the electronic effects of both the Si and Ge shallow donors and the isovalent N impurity. We point out that the mutual passivation effect described herein may be exploited for electrical isolation, band gap engineering, and quantum confinement.

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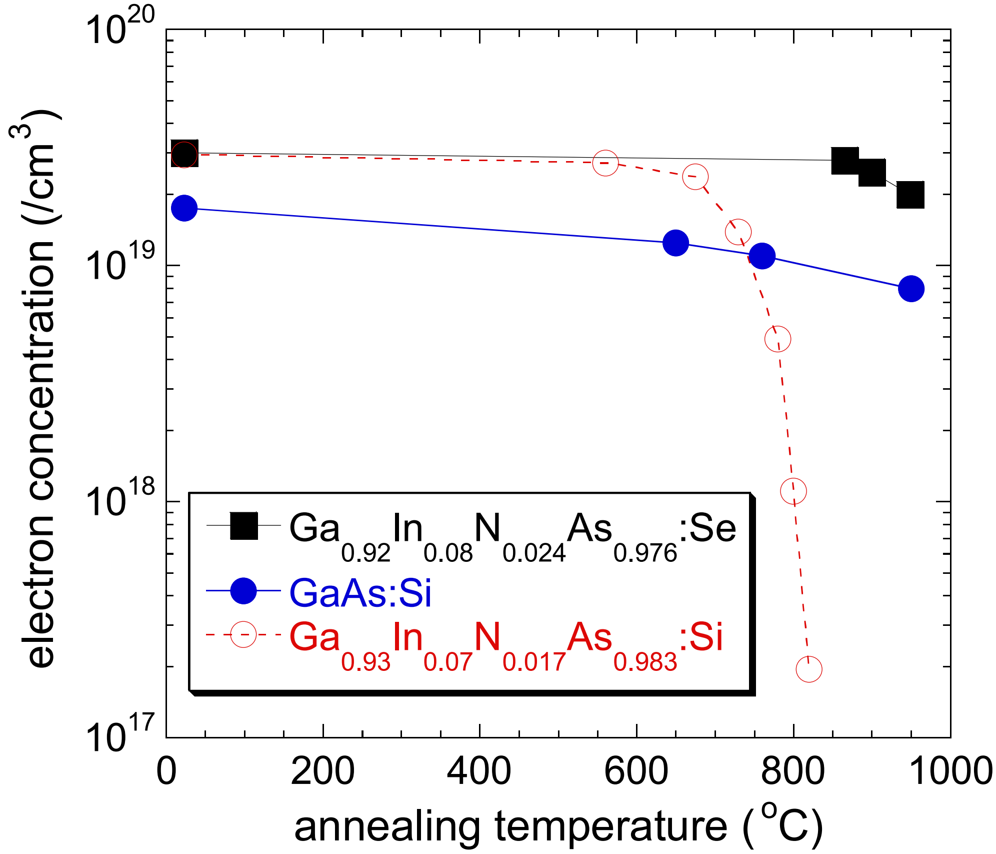
FIGURE CAPTIONS

Fig. 1 Electron concentrations of Si doped GaAs and $Ga_{0.93}In_{0.07}N_{0.017}As_{0.983}$ as a function of annealing temperature for10 s. The dependence of the electron concentration on RTA temperature for a MOCVD-grown Se doped $Ga_{0.92}In_{0.08}N_{0.024}As_{0.976}$ film is also included.

Fig. 2 Normalized free electron concentration as a function of annealing time at different annealing temperatures. The dashed curves represent the results from analytical calculations based on Si diffusion via Ga vacancies.

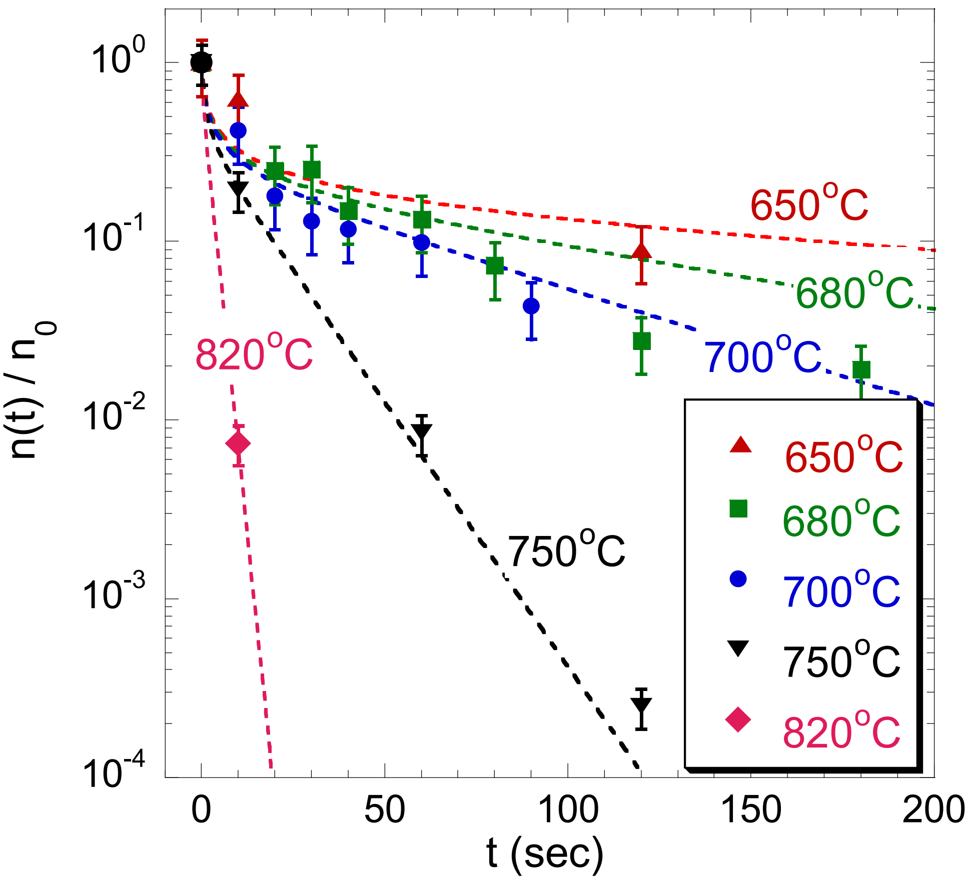
Fig. 3 Photomodulated reflectance (PR) spectra measured from a series of ion beam synthesized Ge doped $GaN_xAs_{1-x}$ samples RTA at 950ºC for durations of 5-120 s. PR spectra from a GaAs wafer. The inset shows the band gap energies determined from the PR measurements.

Fig. 4 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.



electron concentration (/cm3)
10^20
10^19
10^18
10^17
0
200
400
600
800
1000
annealing temperature (oC)
Ga0.92In0.08N0.024As0.976:Se
GaAs:Si
Ga0.93In0.07N0.017As0.983:Si


Fig. 1



n(t) / n0
t (sec)
10^0
10^-1
10^-2
10^-3
10^-4
0
50
100
150
200
650°C
680°C
700°C
750°C
820°C
650°C
680°C
700°C
750°C
820°C


Fig. 2

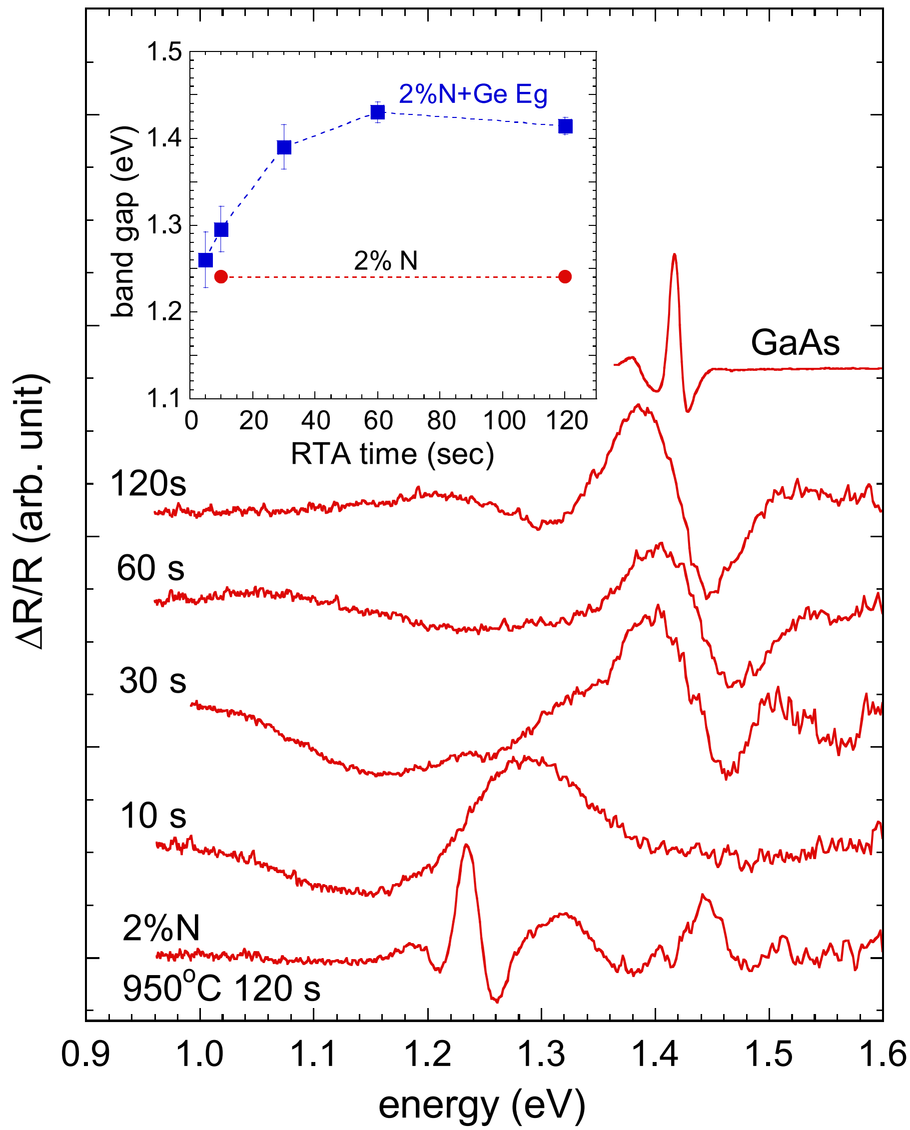

1.5
1.4
1.3
1.2
1.1
band gap (eV)
0
20
40
60
80
100
120
RTA time (sec)
2%N+Ge Eg
2% N
GaAs
120s
60 s
30 s
10 s
2%N
950°C 120 s
ΔR/R (arb. unit)
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
energy (eV)

Fig. 3

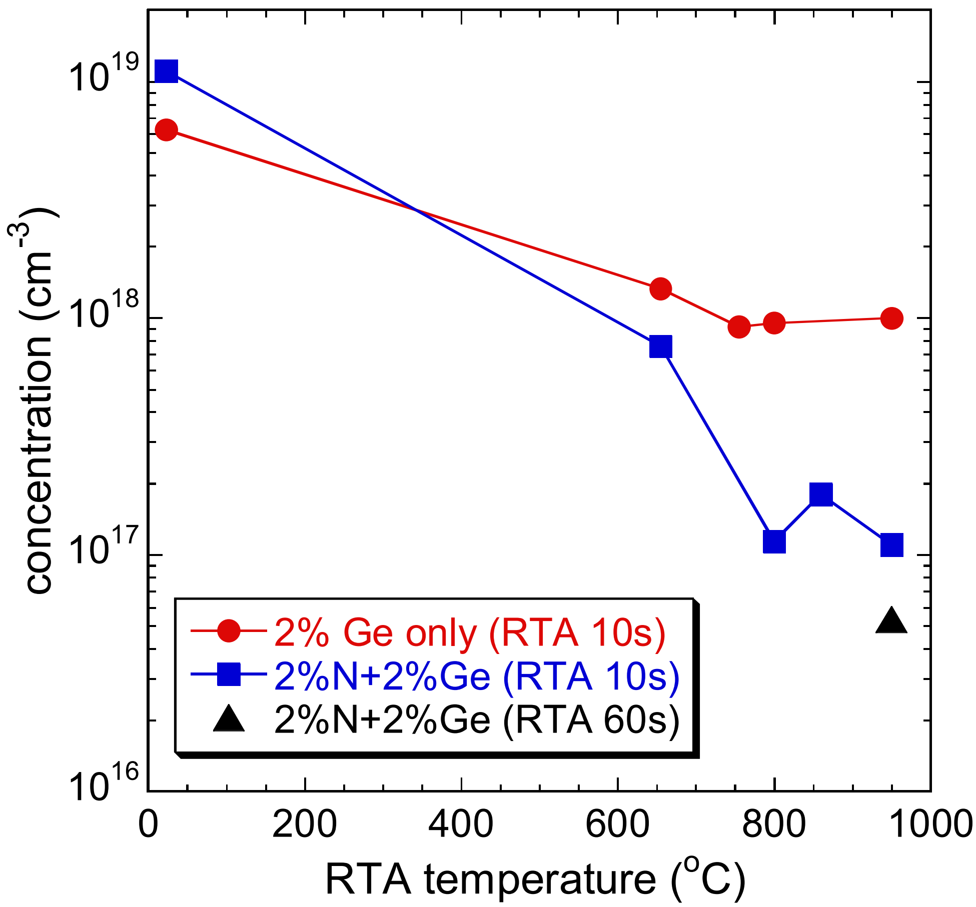

concentration (cm$^{-3}$)
$10^{19}$
$10^{18}$
$10^{17}$
$10^{16}$
0
200
400
600
800
1000
RTA temperature ($^{o}$C)
2% Ge only (RTA 10s)
2%N+2%Ge (RTA 10s)
2%N+2%Ge (RTA 60s)

Fig. 4