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Mutual Passivation of Electrically Active and Isovalent Impurities

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ABSTRACT

We have demonstrated the existence of an entirely new effect in the GaN_xAs_{1-x} alloy system in which the substitutional donor Si and the isovalent atom N passivate each other's electronic activity. This *mutual passivation* occurs in Si doped GaN_xAs_{1-x} through the formation of nearest neighbor Si_{Ga}-N_{As} pairs, is thermally stable up to 950ºC, and correlates with an increase in a sub-band gap, deep level emission at 0.8 eV. Consequently, Si doping in GaN_xAs_{1-x} under equilibrium conditions results in a highly resistive 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 Si concentration. Such mutual passivation is expected to be a general phenomenon for electrically active dopants and localized state impurities that can form nearest neighbor pairs.

Highly mismatched semiconductor alloys (HMAs) in which a small fraction of the metallic anions is replaced by more electronegative elements have become an important class of materials as they exhibit dramatic changes in electronic properties from the host materials giving rise to many potential technological applications.[1-3] A notable and well-studied example is the GaN_xAs_{1-x} HMA, in which 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.[3] The unusual properties of HMAs have been successfully described by the recently proposed band anticrossing (BAC) model.[1,4] The BAC model suggests that an anticrossing interaction between localized states of the foreign electronegative element and the extended states of the host semiconductor matrix splits the conduction band into two subbands. The downward shift of the lower subband is responsible for the reduction of the fundamental band gap while optical transitions from the valence band to the upper subband account for the high-energy edge. This anticrossing interaction also leads to a considerable flattening of the lower subband near its minimum which in turn results in a large increase of the electron effective mass.[1,5] Recent reports have shown that the modified conduction band in GaN_xAs_{1-x} enables an enhancement in the maximum achievable free electron concentration n_{max} by a factor of *five* as compared to GaAs.[6,7] In a heavily Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloy thin film with only 3.3% of nitrogen, maximum free electron concentration n_{max} as high as $7x10^{19}cm^{-3}$ was achieved, more than one order of magnitude larger than that of GaAs.[6]

Polimeni et al. has shown that the introduction of hydrogen into $Ga_{1-y}In_yN_xAs_{1-x}$ and GaN_xAs_{1-x} thin films and quantum wells restores the band gap energy to the values of the materials without N.[8,9] This was attributed to the formation of N-H bonds that resulted in the passivation of N. Subsequent thermal annealing up to 550°C dissociates the N-H bond, completely restoring the band gaps of the diluted nitride layers to their values before hydrogenation. The effects of hydrogenation in this material are very similar to the well-known H passivation of electrically active dopants in

semiconductors.[10] In this paper we demonstrate the existence of an entirely new effect in which an electrically active substitutional Si donor and an isovalent N atom passivate each other's electronic effects. The *mutual passivation* occurs in Si doped GaN_xAs_{1-x} through the formation of nearest neighbor Si_{Ga}-N_{As} pairs when the samples are annealed under conditions such that the diffusion length of Si is greater than or equal to the average distance between Si and N atoms. The passivation is thermally stable up to 950°C and correlates with an increase in a sub-band gap, deep level emission at 0.8 eV.

Two types of GaN_xAs_{1-x} layers were prepared for this study: epitaxial thin films grown by molecular beam epitaxy (MBE) or metal organic vapor phase epitaxy (MOVPE) and N ion synthesized layers. Si dopants were introduced either during the growth or in a post growth Si ion implantation process. The ion synthesized or epitaxially grown samples were either rapid thermally annealed (RTA) or pulsed laser annealed (PLA). RTA was performed in a flowing N_2 ambient in the temperature range of 550-950°C for 1-120 s with the sample surface protected by a blank GaAs wafer. Pulsed laser annealing (PLA) was carried out in air using a XeCl excimer laser (λ=308nm) with pulse duration ~30ns and laser fluences of 0.35- to 0.79 J/cm^2.

The resistivity and free carrier concentration in the samples were measured by the Hall effect technique in the Van de Pauw geometry. Fig. 1 shows the results of Hall effect measurements on a series of MBE-grown $GaN_{0.015}As_{0.985}$:Si and GaAs:Si samples after RTA for 10 sec in the temperature range of 650-950°C. The Si concentration estimated from the growth conditions in these samples is ~$1.6x10^{19}$cm^{-3}. To achieve high donor activation efficiency the samples were typically grown at substrate temperature lower than normal GaAs MBE growth.[11] For the thin film without N, only a slight increase in the resistivity is observed as the RTA temperature increases, corresponding to a decrease in electron concentration, *n* from $1.6x10^{19}$ to $8x10^{18}$cm^{-3} (Fig. 1(b)). Such a decrease in electron concentration in GaAs is in agreement with the amphoteric native defect model that suggests that the equilibrium maximum electron concentration n is in

the range of 10^{18}-10^{19}cm^{-3}.[12,13] The fact that the as-grown GaAs:Si has a high n equals to $1.6\text{x}10^{19}$cm^{-3} indicates that this sample is far from thermodynamic equilibrium, probably due to the highly non-equilibrium nature of the MBE growth process.[11]

In striking contrast to the behavior of the GaAs:Si thin film, the resistivity of the $GaN_{0.015}As_{0.985}$:Si thin films rises drastically at RTA temperatures higher than about 800°C. Correspondingly the free electron concentration in the $GaN_{0.015}As_{0.985}$:Si thin films drops from $1.1\text{x}10^{19}$cm^{-3} in the as-grown film to $3\text{x}10^{17}$cm^{-3} in the film RTA at 950°C. In fact, RTA at 950°C for longer time durations further reduces the free electron concentration in the $GaN_{0.015}As_{0.985}$ sample (to $n < 10^{15}$cm^{-3} for 120sec) while no significant change is observed in the GaAs sample.

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 from the Si donors and isovalent N atoms. 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.

To test this hypothesis we have investigated the annealing behavior of a Se doped MOVPE-grown $GaN_{0.012}As_{0.988}$ thin film with Se concentration of $\sim 4\text{x}10^{20}$cm^{-3}. As is shown in Fig. 1 (b) only a small decrease of electron concentration is observed in this Se doped sample after annealing at 950°C, similar to the behavior found in the GaAs:Si sample. We also note that no passivation effects can be observed for S donors in S implanted GaN_xAs_{1-x} thin films.[7] This result clearly supports our conjecture that N in GaN_xAs_{1-x} cannot passivate group VI donors because N_{As} *does not* reside in the nearest neighbor of a VI_{As} donor (such as Se or S).

The results in Fig. 1 indicate that the thermally activated passivation has a relatively well-defined onset temperature of about 800°C. This can be understood assuming that the passivation process is controlled by the diffusion of randomly

distributed Si atoms to a Ga site with a N_{As} nearest neighbor. It has been shown that the diffusion constant of Si in GaAs is well described by the formula $D=D_0\exp(-E_a/kT)$ with $D_0=4\times10^{-4}$ cm^2 and $E_a=2.45$ eV.[14] Using this formula, we find that annealing for 10 sec at 780°C is required for Si atom diffusion length $L_D=(Dt)^{1/2}$ to be equal to the average distance of ~9 Å from a Si atom to its nearest N site in $GaN_{0.015}As_{0.985}$. This temperature is very close to the observed onset of the Si passivation shown in Fig. 1. It should be noted that any rearrangement of N atoms should be negligible because of their much higher diffusion activation energy of 3.6 eV.[15]

Further support for the notion of the Si diffusion controlled passivation is provided by thermal annealing of a thin film $Ga_{1-y}In_yN_xAs_{1-x}$:Si alloy (x=0.017, y=0.07) with a much higher Si concentration of ~9×10^{19}cm^{-3} and an electron concentration of 3×10^{19}cm^{-3}. As is shown in Fig. 1(b), the onset of the passivation in this sample with much higher Si concentration occurs at a lower temperature of about 700°C. Since the Si diffusion is mediated by triply negatively charged gallium vacancies V_{Ga}^{3-} the activation energy for the diffusion process depends on the Fermi energy.[16] The increase of the electron concentration from 1.1×10^{19} cm^{-3} in the $GaN_{0.015}As_{0.985}$ sample to 3×10^{19}cm^{-3} in the $Ga_{0.97}In_{0.03}N_{0.01}As_{0.99}$ sample shifts the Fermi energy by $\Delta E_F=0.09$ eV, resulting in a reduction of the diffusion activation energy by $3\Delta E_F=0.27$ eV, or $E_a=2.18$ eV. Using this value of E_a, we obtain a Si diffusion length that equals the average separation of 8.6Å between Si donors and nearest N atoms for annealing at about 670°C for 10sec. This temperature is again in very good agreement with the observed onset of the Si passivation in the $Ga_{0.97}In_{0.03}N_{0.01}As_{0.99}$ alloy film.

The above results provide compelling evidence that the formation of Si_{Ga}-N_{As} is responsible for the elimination of the shallow dopant behavior of Si atoms. However, since the isovalent nitrogen is responsible for a massive modification of the electronic structure of GaN_xAs_{1-x} alloys,[1,4] the extent to which the formation of these pairs affects the role of N atoms in the alloys is investigated. The most straightforward and reliable

way to determine the concentration of active N atoms is to measure the width of the fundamental band gap, which is related to the concentration of the active N atoms through the expression derived from the band anticrossing model.[1,4] The band gap of the films was measured using photomodulated reflectance (PR) at room temperature using a chopped HeCd laser beam (λ=442 nm or 325nm).[2] Fig. 2 shows the effect of thermal annealing on the band gap of two $Ga_{0.93}In_{0.07}N_{0.017}As_{0.983}$:Si samples with Si concentration of ~$1.6x10^{19}$ and $9x10^{19}cm^{-3}$. We note that the electrical behavior of the sample with [Si]~$1.6x10^{19}cm^{-3}$ as a function of annealing is identical to that of the GaN_xAs_{1-x}:Si sample shown in Fig. 1. The annealing has a very small effect on the band gap of the sample doped with lower Si concentration. This is not unexpected due to the relatively low total Si concentration of ~$1.6x10^{19}cm^{-3}$ (corresponding to only 0.07% molar fraction). Passivation of this low concentration of N atoms would change the band gap by less than 10 meV.

In contrast, thermal annealing results in a considerable widening of the energy gap in the $Ga_{1-y}In_yN_xAs_{1-x}$ sample doped with ~$9x10^{19}cm^{-3}$ Si atoms. Annealing of the sample at 950°C increases the gap by about 35 meV. This increase in band gap corresponds to a reduction of the concentration of the active N atoms by $8x10^{19}cm^{-3}$. The reduction in active N is very close to the total Si concentration. This confirms that the formation of Si_{Ga}-N_{As} pairs results in a *mutual passivation* of both species: it eliminates the electrical activity of Si donors and deactivates N as the isovalent dopant. As has been discussed above it appears that the Si_{Ga}-N_{As} pair strongly binds the fourth valence electron of Si, transforming this shallow hydrogenic donor into a deep localized center.

This scenario of the passivation process is further corroborated by photoluminescence (PL) measurements on the $GaN_{0.015}As_{0.985}$:Si sample. The PL signals were generated in the backscattering geometry by excitation with the 515 nm line of an argon laser. The signals were then dispersed by a SPEX 1680B monochromator and detected by a liquid-nitrogen cooled Ge photodiode. Fig. 3 shows room temperature

(295K) and low temperature (12 K) PL spectra for samples annealed at different temperatures. The room temperature PL spectrum of the as-grown sample shows a broad band edge peak at 1.15 eV and weaker deep luminescence feature at about 0.8 eV. It is clearly seen from the results in Fig. 3 that annealing at temperatures higher than 800°C results in a strong increase of the intensity of the low energy PL peak at 0.8eV. At the same time the intensity of the band edge PL is drastically reduced and is not detectable in the sample annealed at 950°C. Comparing these results with the results of Fig. 1 we find a clear correlation between decreased electrical activity of Si donors and an increased deep level luminescence, strongly suggesting that the deep PL is associated with Si_{Ga}-N_{As} pairs.

The discovered *mutual passivation* of Si and N in GaAs represents a unique effect that could be used to locally control the band structure and/or electrical properties of materials. In order to test the feasibility of this approach we have also studied the mutual passivation in N and Si co-implanted GaAs. Recently we have reported the successful synthesis of GaN_xAs_{1-x} thin films by N-implantation in GaAs followed by a combination of pulsed laser annealing (PLA) and RTA.[17] Using this method we have synthesized GaN_xAs_{1-x} layer with x as high as 0.016. Using the same technique we formed Si doped GaN_xAs_{1-x} layers by sequential implantation of N and Si ions into a semi-insulating GaAs wafer at room temperature followed by PLA and RTA. The multiple-energy N+Si implantation created a ~0.3 µm thick layer with N concentrations ~3.6×10^{20} cm^{-3}. The top ~0.25 µm of this layer was implanted with a uniform Si concentration of ~6.3×10^{19} cm^{-3}.

Fig. 4 shows the PR spectra from the Si doped and undoped GaN_xAs_{1-x} samples after PLA with a laser fluence of $0.4 J/cm^2$ followed by RTA at 950°C for 10s. The undoped layer was synthesized by the N implantation alone. The sample implanted with N alone showed a PR transition at 1.25eV, a band gap reduction of 160meV compared to the GaAs substrate. Using the BAC model, this corresponds to a GaN mole fraction (x)

of 0.0088. PR measurement on the Si doped GaN_xAs_{1-x} sample reveals a band gap of 1.29eV, corresponding to x=0.006. The larger band gap of the Si doped GaN_xAs_{1-x} layers (by 40meV) as compared to the undoped sample shown in Fig. 4 can be attributed to a reduction of N concentration by ~$6x10^{19}cm^{-3}$, a value similar to the implanted Si concentration in the layer. At the same time, electrical measurements reveal that the N+Si layer is very resistive with contact resistance in the MΩ range indicating that all Si donors are passivated by forming Si_{Ga}-N_{As} pairs.

In conclusion, we have discovered the *mutual passivation* for electrically active (Si) and isovalent (N) in GaAs. Our experimental results provide strong evidence that this mutual passivation is due to the formation of Si_{Ga}-N_{As} bonds that are thermally stable. Consequently, Si doping in GaN_xAs_{1-x} results in a highly resistive GaN_xAs_{1-x} layer with fundamental band gap governed by a net "active" N (roughly equal to the total N content minus the Si concentration). We expect that such mutual passivation is a general phenomenon for electrically active hydrogenic dopants and impurities that form localized states when these species reside in cation and anion sites of the semiconductor so that they can form nearest neighbor passivating pairs, e.g. other group IV donors (Ge and Sn) in GaN_xAs_{1-x}. This mutual passivation of electrically active and isovalent impurities in compound semiconductors can be exploited for electrical isolation, band gap engineering and quantum confinement. This also provides a unique opportunity for the fabrication of both planar and three-dimensional novel structures by the selective implantation of either one or both species.

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FIGURE CAPTIONS

Fig. 1 Resistivities (a) and electron concentrations (b) of GaAs:Si and $GaN_{0.015}As_{0.985}$ as a function of annealing temperature for10 sec. The Si concentration in these films is ~$1.6x10^{19}cm^{-3}$. The dependence of electron concentration on annealing temperature (for 10sec) for a $Ga_{0.93}In_{0.03}N_{0.017}As_{0.93}$ film doped with ~$9x10^{19}cm^{-3}$ Si atoms and a Se doped MOCVD-grown $GaN_{0.012}As_{0.988}$ film are also included in 1(b).

Fig. 2 The band gap energies of two $Ga_{0.93}In_{0.03}N_{0.017}As_{0.93}$ films doped with ~$1.6x10^{19}cm^{-3}$ and $9x10^{19}cm^{-3}$ Si atoms measured by photomodulated reflectance (PR) as a function of 10 sec rapid thermal annealing (RTA) temperature.

Fig. 3 Photoluminescence (PL) measurements at room temperature (dotted spectra) and 12K (solid spectra) from $GaN_{0.015}As_{0.95}$ thin films doped with ~$1.6x10^{19}cm^{-3}$ Si atoms.

Fig. 4 PR spectra from Si-doped and undoped GaN_xAs_{1-x} samples synthesized by N+Si and only N implantation, respectively, after PLA with a laser fluence of $0.4J/cm^2$ followed by RTA at 950°C for 10s.

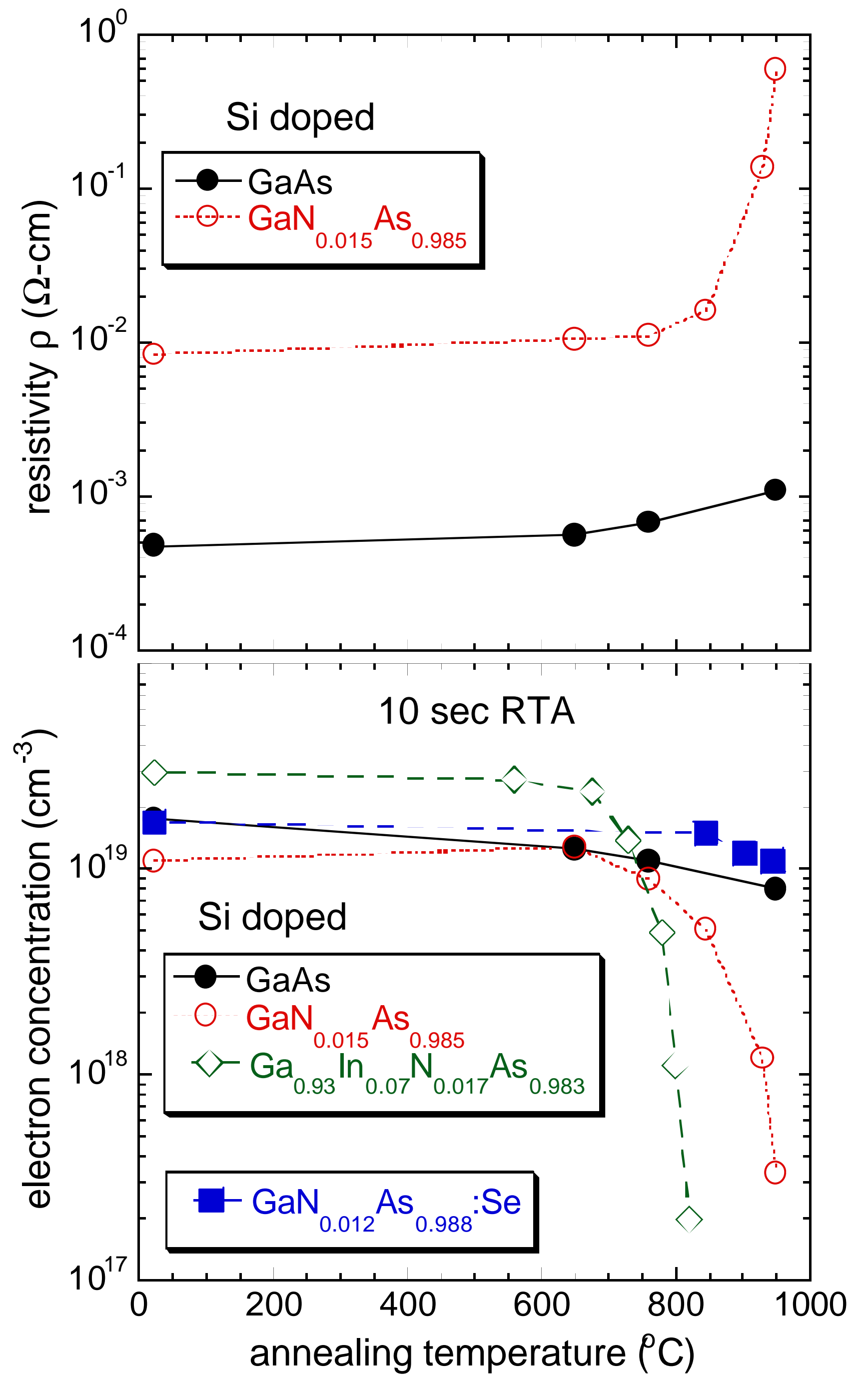

Fig. 1

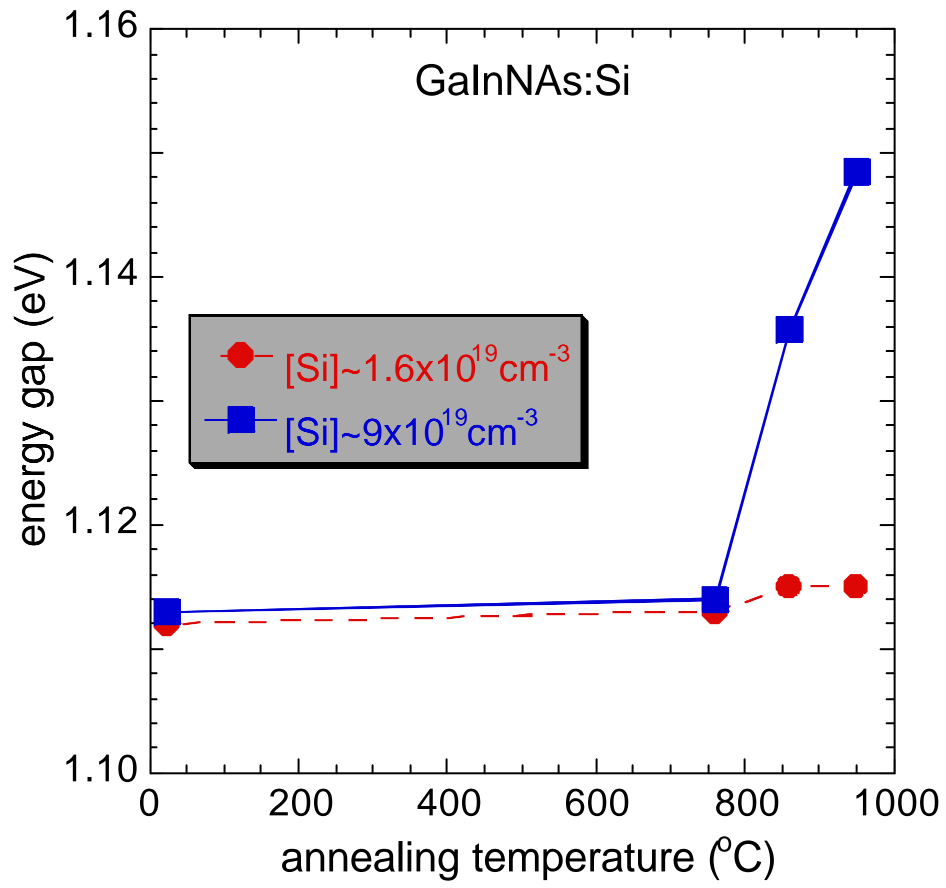

Fig. 2

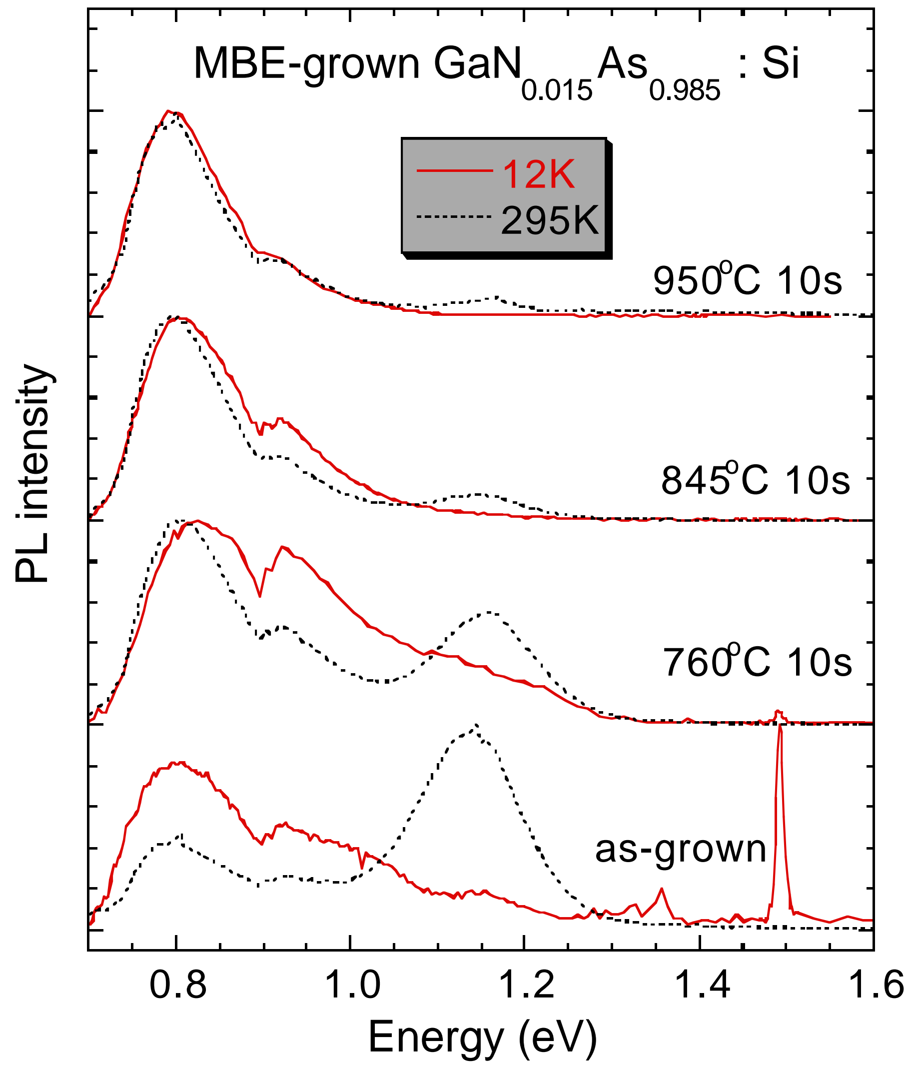

Fig. 3

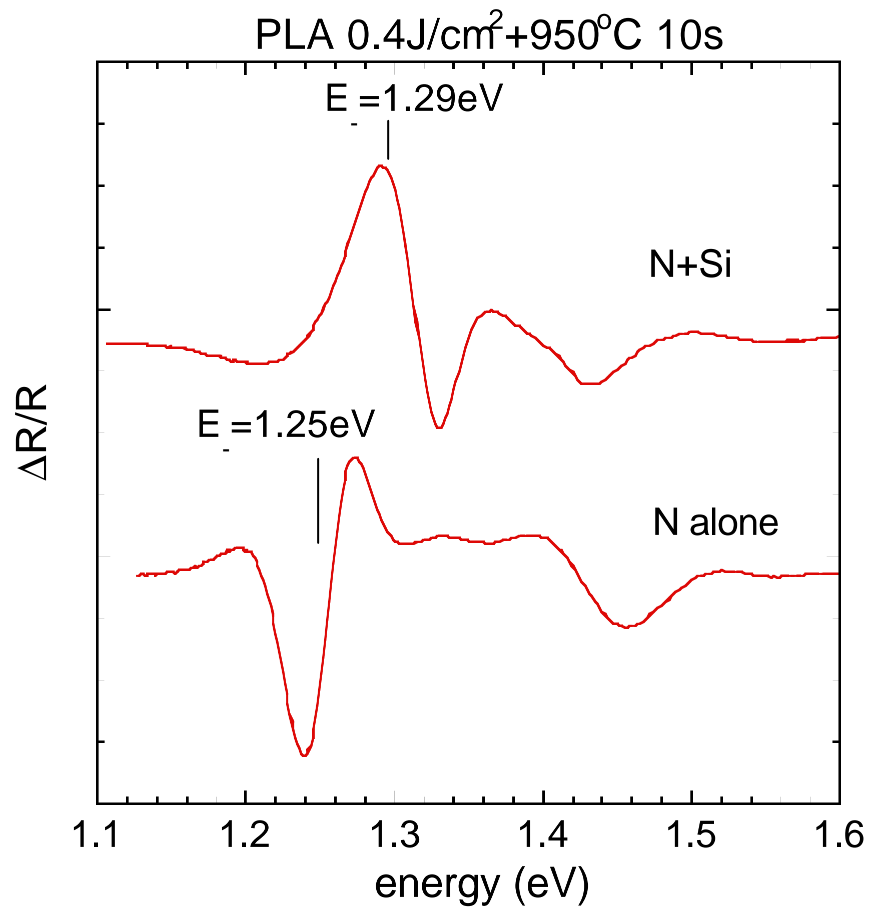

Fig. 4