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Growth orientation dependence of Si doping in GaAsN

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The incorporation of Si in GaAsN alloys grown simultaneously on (100), (311)A, (311)B, and (211)B GaAs substrates by the chemical beam epitaxy has been investigated. The decrease in electron concentration with the increasing N composition suggests the occurrence of N and Si interaction, whereas the interaction exhibits evidently different extent depending on the growth orientation. Combined with the secondary ion mass spectrometry and photoluminescence measurements, it is revealed that (311)B and (211)B are the promising substrate orientations to reduce the N-Si passivation and improve n-type Si doping in GaAsN over a wider N composition range. A surface bonding model is utilized to explain the plane polarity dependent incorporation behaviors of Si and N. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4907389]

I. INTRODUCTION

Employment of controllable p-type and n-type doping in one semiconductor is essential to construct the pn-junction solar cells. Silicon is a widely used dopant in the epitaxy of III-V compound semiconductors. Its doping physics have been well studied theoretically and experimentally in GaAs during last decades, and to a much less extent in Ga(In)AsN, a promising material of high-efficiency multijunction solar cells.[1] Novel incorporation behaviors of Si donor including the remarkably weakened electrical activity were revealed in Si-doped GaAsN and attributed to the mutual passivation between Si and N.[2–5] The presumable formation of Si_{Ga}-N_{As} pair, which transforms the Si shallow donor into a deep localized center, was suggested in early experimental reports and theoretical predictions.[2,6] In their recent first-principle calculation,[7] however, Janotti *et al*. applied the true GaAsN conduction-band minimum (CBM) instead of the GaAs CBM as the reference and found that N and Si in fact combine into a deep-acceptor split interstitial $(Si\text{-}N)_{As}$ with a much lower formation energy than that of the Si_{Ga}-N_{As} pair in GaAsN alloys. Intensive experimental work is thus desirable to clarify the debate.[4] On the other hand, most work on improving GaAsN alloy quality has been restricted to the traditional growth orientation (100). We have recently shown that intentionally engineering the crystallographic orientation for GaAsN growth facilitates the preferential incorporation of interested adatoms.[8,9] N incorporation in GaAsN can be significantly enhanced on (311)B GaAs substrate while maintaining impressive carrier lifetime as compared with (100) GaAsN layers.[9,10] Many pioneering studies on GaAs:Si epitaxy have discovered that competitions among incoming Si, Ga, and As adatoms can be effectively altered by changing the growth orientation and/or surface polarity, and eventually influences the Si doping efficiency as a donor at Ga site or an acceptor at As site.[11–13] One would expect that attractive Si-doping phenomena on crystallographic orientations other than (100) might be helpful to improve Si doping efficiency in GaAsN and further understand the Si-N interactions as well. In this paper, we report our studies on the Si doping behavior in GaAsN epilayers on (100), (311)A, (311) B and (211)B GaAs substrates. Effects of the growth orientations were discussed based on the atomic bonding geometries at the epitaxial surface. Our results suggested that the (311)B and (211)B GaAs are the favored substrates to reduce the N-Si mutual passivation and achieve efficient Si doping as donors in GaAsN.

II. EXPERIMENTAL

The GaAsN alloys of ~1 μm thick were grown simultaneously side by side on (311)A/B, (211) B, and (100) GaAs substrates by the chemical beam epitaxy (CBE) system. The atomic arrangement of the ideal (n11) substrate surface can be viewed as composed of ⟨100⟩ and ⟨111⟩ components. As illustrated in Fig. 1, the corresponding ⟨111⟩ and ⟨100⟩ component ratios are 2:1 and 1:1 for (211) and (311) substrates, respectively. Triethylgallium (TEGa), trisdimethylaminoarsenic (TDMAAs) and monomethylhydrazine (MMHy) were used as Ga, As, and N sources in our CBE system. Si doping was achieved via a constant supply of 0.7 sccm SiH_4 gas during the growth. Flow rates of TEGa and TDMAAs were fixed to 0.1 and 1.0 sccm, respectively, while MMHy flow rate was varied as 0, 4, 6, 9, and 11 sccm to examine the effect of N composition on the Si incorporation. The growth temperature is 460 °C. High resolution X-ray diffraction (HRXRD) was measured via Philips X'pert Pro diffractometer. $2\theta/\omega$ scan of (422), (311), and (400) reflections were performed on (211), (311), and (100) samples, respectively.

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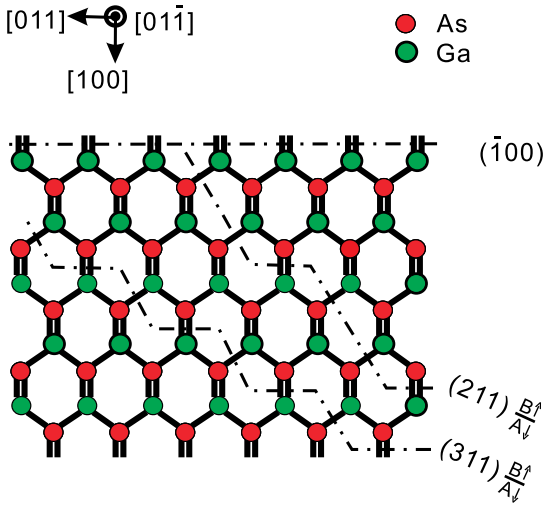

FIG. 1. Schematic illustration of atomic structures of (100), (211), and (311) GaAs planes.

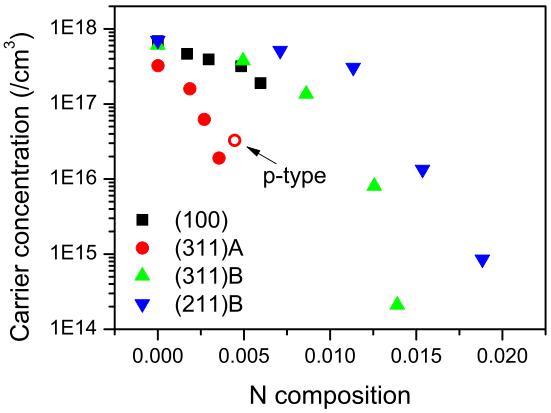

FIG. 2. Free carrier concentration as a function of the N composition in GaAsN:Si with different growth orientations. The solid symbols are for the electron, and the open one for the hole. Note that depending on the growth orientation, the N composition spreads across different ranges despite of the parallel growths.

N composition was determined from Bragg angles of the GaAs and GaAsN reflections.[14] To conduct Hall effect measurement, evaporated In was annealed at 350 °C in N_2 for 5 min to form the Van der Pauw configuration. Continuous wave (cw) PL measurement was excited by a 532 nm line of the LD-pumped neodymium-doped yttrium orthovanadate ($Nd:YVO_4$) laser. The actual atomic concentrations of Si and N were examined by secondary ion mass spectrometry (SIMS) on the samples with a multilayer structure. The growth of the multilayer starts with a GaAs:Si layer, which is followed by three circles of GaAsN:Si/GaAs:Si growth with 4, 6, and 9 sccm N precursor flow rate applied for the N containing layers. The other growth parameters for each GaAsN:Si sublayer were reproduced from the respective Hall effect samples. It renders the multilayer structure quite convenient to get the complete componential variation as a function of the N precursor flow rate on single sample for each orientation.

III. RESULTS AND DISCUSSION

Figure 2 presents the carrier concentration as a function of N composition for GaAsN:Si films with different growth orientation. Although parallel growths were conducted in one run for each N flow rate, substrate orientation leads to remarkable deviations in the final N composition in GaAsN as we have reported elsewhere.[8,9] The enhanced incorporation of N in (n11)B GaAsN is believed to be a direct consequence of the peculiar three-dangling-bond (TDB) V sites on (n11)B growing surface, which is energetically favorable for N adatoms due to its larger electronnegativity relative to As. Higher density of such TDB V sites on (211)B as compared to (311)B further strengthen their contributions, while the TDB III sites on (311)A have no contributions to the N incorporation as expected. The n-type conductivity can be seen in GaAs:Si regardless of the substrate orientation, and III site is thus the preferred occupation site for Si as N not involved. The relatively low electron concentration in (311)A GaAs originates from the fact that the TDB feature of III site on (311)A surface reduces the Si occupying opportunity, because the metallic Ga wins out during the competition and readily forms stronger bond with As. The above findings agree well with the SIMS measurement results on atomic concentration, as illustrated in Fig. 3: the highest N atomic concentration occurs in (211)B sample, while the

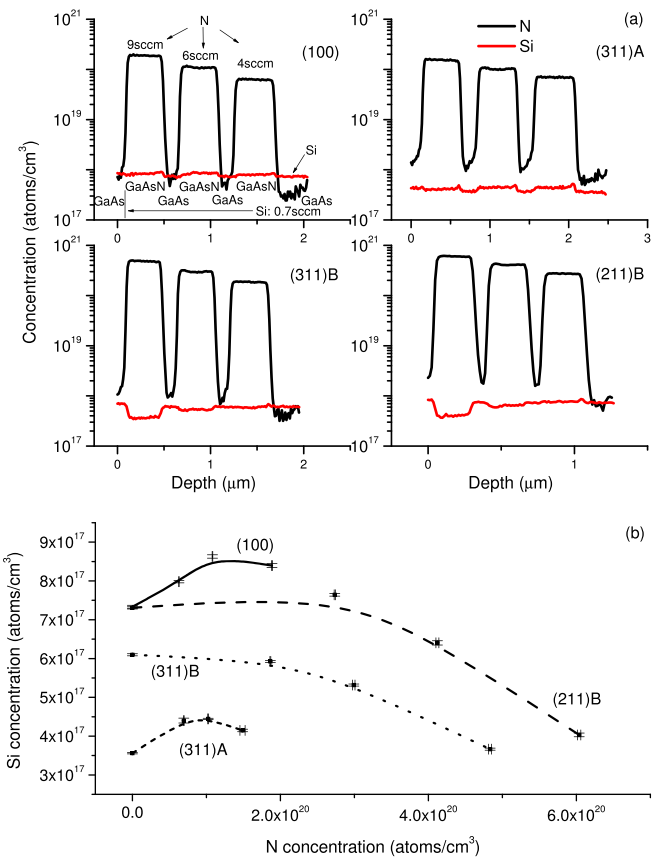

FIG. 3. (a) Nitrogen and silicon concentration profile of GaAsN:Si multilayers grown on different GaAs substrates. In the multilayer structure, three GaAsN:Si layers with 4, 6, and 9 sccm N precursor flow rate are separated by GaAs:Si spacers. A constant SiH_4 supply of 0.7 sccm was applied to achieve the Si doping. (b) Silicon concentration as a function of nitrogen incorporation based on the SIMS results in (a).

lowest one is found in (311)A GaAsN for each growth circle; and Si atomic concentration is evidently lower in (311)A GaAs in contrast to the levels in GaAs samples with other orientations.

The N composition dependencies of free carrier concentration are quite different for adopted orientations, as illustrated in Fig. 2. The deactivation of Si doping does accompany even a small amount of N introduction for all samples, which is consistent with the previous reports.[5] However, the decreasing extent is evidently different. A rapid declining tendency of free carrier level occurs for (311)A sample within a relatively narrow N composition range, implying a much stronger interaction between Si and N. Such an enhanced Si-N interaction finds supports from the SIMS measurement results (Fig. 3): in contrast to the continuous reduction of the free electron level, (1) the atomic concentration of Si slightly increases after the introduction of N into GaAs; (2) Si atomic concentration in GaAsN remains the comparable level with the increasing N composition. As analyzed above, both N and Si adatoms have limited opportunities to incorporate into (311)A GaAs due to the abundant existence of the TDB III site. This in turn increases the chances for the reactions between those two elements to form N-Si complex near the growth surface even in the vapor phase. Such a reaction with N to certain extent drives Si doping presumably as a form of N-Si complex to occupy As sites, which explains the deactivation of Si donors and the slight increase of atomic Si level in GaAsN relative to GaAs. Further increasing N incorporation finally leads to the p-type conductivity of (311)A GaAsN:Si simply due to the significant N-Si reaction. The hole concentration almost reaches the level of our undoped GaAsN with H-complex or residual C as potential acceptors. The assumption that $(\text{N-Si})_{\text{As}}$ is the likely form of the dominant complex agrees with the prediction of Jin *et al* based on their experiments,[4] though more direct evidences are necessary. In their theoretical model,[7] Janatti *et al*. calculated the local vibrational mode associated with $(\text{Si-N})_{\text{As}}$ interstitials and predicted the occurrence of the Si-N stretch mode at $\sim 935\,\text{cm}^{-1}$. In an attempt to identify the Si-N complex form and also evaluate its relative concentration via the related peak intensity, we performed the Fourier-transform infrared (FTIR) measurement. Eventually, it was found that the characteristic frequency for $(\text{Si-N})_{\text{As}}$ is quite close to the second harmonic mode peak ($\sim 940\,\text{cm}^{-1}$) of N at the As site (N_{As}) and the wagging mode peak ($\sim 960\,\text{cm}^{-1}$) of N–H related defects in CBE grown GaAsN.[15,16] That renders the accurate identification of Si-N complex quite difficult in experiment. We think that might also be the reason that the debates on the formation of Si-N are mainly based on the theoretical calculation up to now.

A quite moderate reduction rate of free electrons is recorded in GaAsN layers with B polar surface for the N composition lower than 0.01 (see Fig. 2, corresponding to the N source flow rate of ~4 sccm). This can be explained by the fact that the N adatom has the superiority over the (N-Si) complex to occupy TDB V sites on the (n11)B growth surface. As a result, the N incorporation does not cause remarkable increase in Si atomic concentration for (311)B and (211)B samples as observed in (100) and (311)A samples (see Fig. 3). On the contrary, dramatic atomic decrease takes place as the N source flow rate rises above 4 sccm. Note that similar phenomena were not observed or at least not remarkable in (311)A and (100) samples at the same N source supply level. The increasing supply of N facilitates the formation of (N-Si) complex on the growth surface, which cannot efficiently incorporate into As site on (n11)B surface on one hand, and inevitably decreases the amount of Si into the Ga site as an active donor on the other hand. A remarkable drop of the free electron level starts therefore at the very high N composition in (311)B and (211)B samples. However, it should be notified that the doping efficiency of Si as a donor in GaAsN with B polar growth surface is clearly superior to that with (100) and A polar surface. The conversion of conductivity type does not occur even at high N incorporation level for (311)B and (211)B GaAsN.

Another distinct feature accompanying Si doping in GaAsN is the weakened effect of N on the GaAsN bandgap because the passivation has been proved to be mutual.[2,7] The room-temperature PL spectra for (211)B and (311)A GaAsN layers are demonstrated in Fig. 4(a) to collect evidences from the possible bandgap variations. Fig. 4(b) compares the peak energy of band edge emission vs N composition with the calculation results based on the band anticrossing (BAC) model.[17] Experimental dots of (211)B sample are seen to trace the theoretical tendency almost up to a high N content of 1.54%, which means that benefiting from the relatively weak N-Si interaction on (n11)B polar planes, the passivation effect could be refrained to a wider N composition range. In contrast, the measured bandgap of (311)A sample clearly deviates to the higher energy side of the theoretical line at lower N incorporation level. For the N composition of ~0.36% in (311)A, an energy difference between experiment

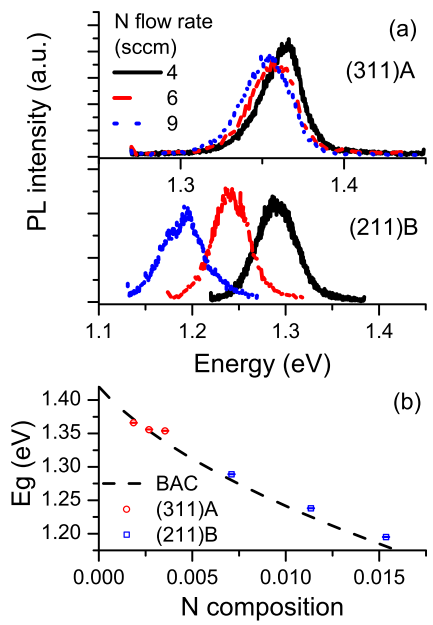

FIG. 4. (a) PL spectra of (311)A and (211)B GaAsN:Si layers with different N incorporation; (b) energy gap of GaAsN layers as a function of N content. The symbols are band edge emission energy deduced from experimental data in (a). The dashed line in (b) is the theoretical value based on the band anticrossing model with a coupling parameter of 2.7 eV.

and theory is recorded to be ~18 meV. The energy deviation also tends to rise for (211)B sample with increasing N content. The measured deviation value of ~13 meV at a high N level of ~1.54%, however, is still lower than that in the (311)A GaAsN with N composition less than one quarter of (211)B. Thus, the relaxation of N effect on the bandgap is quite evident in (311)A sample. These optical observations are in good agreement with the electrical results, which suggests that epitaxial growth of GaAsN layer on B polar GaAs substrate might be a potential choice. Finally, it should be noted that the assumption of the ideal (n11) A/B surface made in the discussion is likely to be oversimplification, but we would expect similar bonding differences with similar consequences to occur also on real (n11) A/B surfaces. Simple model facilitates to provide the basic guidance and clear picture in explaining novel experimental findings on N and Si incorporation, as has been generally adopted in the pioneering work on Si doping on high-index GaAs planes.[11,12] On the other hand, a theoretical model to exactly describe the GaAsN growth mode by including the surface reconstruction factors is believed helpful in explaining the observed effect of growth orientation on the formation of N-related defects in experiment. The related work is still in process and will be presented in detail elsewhere.

IV. CONCLUSIONS

In summary, we have studied the doping behavior of Si in GaAsN growing on (100), (311)A/B, and (211)B GaAs substrates. (311)B and (211)B GaAs were found to be the potential substrates to promote Si doping efficiency as a n-type dopant in a wider N composition range, while (311)A substrate deteriorates it. The different interaction extent between Si and N, which originates from the polar features of three-dangling-bond surface site, is considered to account for the phenomena.

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