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The Effect of Self-Diffusion on the Zn Diffusion in III-V Compound Semiconductors

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Abstract: Zn diffusion in III-V compound semiconductors are commonly processed under group V-atoms rich conditions because the vapor pressure of group V-atoms is relatively high. In this paper, we found that group V-atoms in the diffusion sources would not change the shaped of Zn profiles, while the Zn diffusion would change dramatically under group III-atoms rich conditions. The Zn diffusions were investigated in typical III-V semiconductors: GaAs, GaSb and InAs. We found that under group V-atoms rich or pure Zn conditions, the double-hump Zn profiles would be formed in all materials except In As. While under group III-atoms rich conditions, single-hump Zn profiles would be formed in all materials. Detailed diffusion models were established to explain the Zn diffusion process; the surface self-diffusion of matrix atoms is the origin of the abnormal Zn diffusion phenomenon.

Keywords: Zn Diffusion, Self-Diffusion, III-V Compound Semiconductors

1. Introduction

Zn diffusion into III-V compound semiconductor is an important process for fabrication of junction field-effect transistors [1], thermophotovoltaic (TPV) cells [2-5] and infrared detectors [6]. The shape of Zn profiles has a direct impact on device performance. However, under constant Zn pressure, Zn profiles in III-V semiconductors don't follow the complementary error function [7], distorted phenomenon occurred in Zn profiles [1-2]; it is difficult to predict the precise diffusion profiles. During Zn diffusion process, the self-diffusion of matrix atoms occurred at the same time, thus the self-diffusion should be taken into account during Zn diffusion.

Take typical III-V semiconductor - GaAs for example, the vapor pressure of As is higher than the Ga, thus the As atoms are commonly added into the diffusion source. Under As-rich conditions, the double-hump Zn profile is obtained in GaAs [1]. In this paper, we found that if Ga atoms were added into the diffusion source, the first hump in Zn profile was "removed". Based on the above phenomenon, the investigations were extended to the materials of GaSb and InAs. The surface self-diffusion of matrix atoms should be responsible for the abnormal Zn diffusion phenomenon, details about our experiments and analyses are presented below.

2. Experimental Procedure

The n-type GaSb and InAs wafers were selected for the experiments. There are several internal defects such as Si_{As} acceptors, Si clusters, and Si_{Ga}-Ga vacancy complexes in n-GaAs which would have effect on Zn diffusion [10], thus the semi-insulating GaAs with little defects was selected. The specific parameters of wafers and the diffusion sources are listed in Table 1; the purity of all the diffusion sources is 99.9999%.

Table 1. *Parameters of wafers and diffusion sources used for experiments.*

Wafer	Doping/ orientation	Diffusion sources		
		Pure Zn	III-atoms rich	V-atoms rich
GaAs	Semi-insulating <100> -oriented	Zn	Zn -Ga (3wt%Zn)	Zn -As (Zn_3Sb_2)
GaSb	Te-doped (n-type) <100> -oriented	Zn	Zn -Ga (3wt%Zn)	Zn -Sb (Zn_3Sb_2)
InAs	S-doped (n-type) <100> -oriented	Zn	Zn -In (3wt%Zn)	n/a

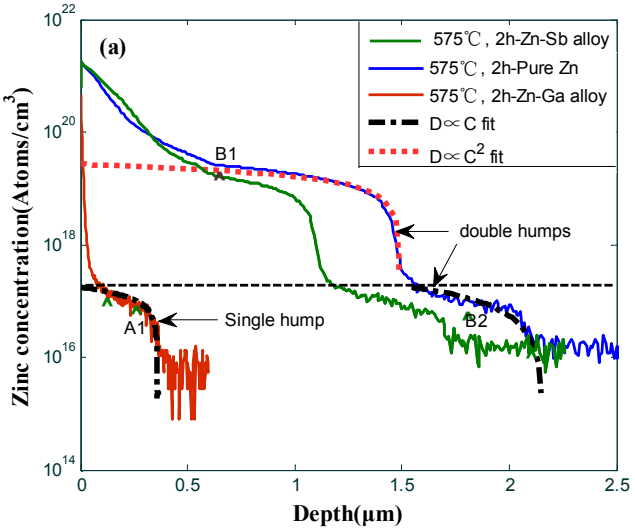
Zn diffusion experiments were performed in vacuum sealed ampoules. The sealed ampoules were placed in a small-sized OTF-1200X tube furnace with the temperature control accuracy of ±2K. The rate of temperature increase was set at 10K/min. After the diffusion process, the ampoules were quickly pulled out from the tube furnace and cooled in N_2. Zn profiles in all semiconductors were measured using CAMECA IMS4F SIMS (secondary-ion-mass spectrometry).

3. Experimental Results and Analysis

3.1. Zn Diffusion in GaAs

Figure 1a shows the Zn profiles using Zn, Zn-Ga and Zn-As alloy sources. Clear disparities can be found. Under pure Zn condition, the Zn profile has double humps; while under Ga-rich condition, the Zn profile has only a single hump, the first hump has been "removed". We found that $D \propto C$ (D:Zn diffusion coefficient, C: Zn diffusion coefficient) is fit for the main region of the single-hump profile and the second hump of double-hump profile; while $D \propto C^2$ is fit for the first hump of the double-hump profile.

The Zn-As alloy is commonly used for the diffusion source due to the high pressure of As [11], while our experimental results showed that the As-rich condition was similar to that of pure Zn. The As atoms in the diffusion sources can only shorten the first hump of the double-hump profile.



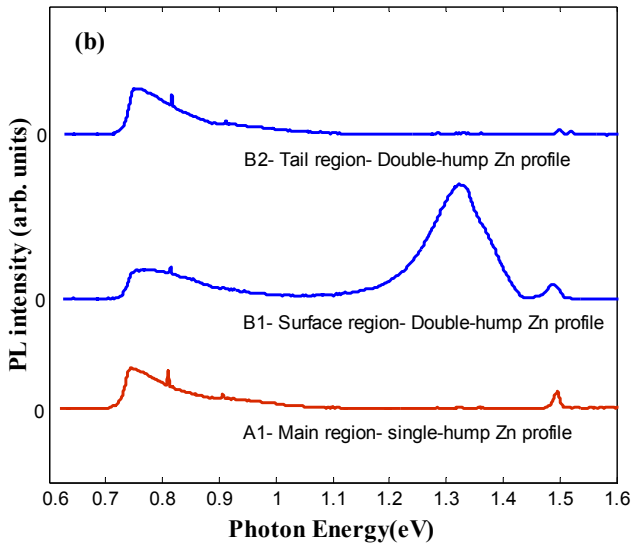


Figure 1. *(a) Zn profiles in GaAs with different sources and simulations. (b) PL spectra at 15K at the point of A1, B1 and B2.*

Figure 1b shows the PL peaks at different etching depth. The main region of single-hump profile (A1) showed the similar PL peaks with the second hump of double-hump profile (B2). The PL peaks at 0.75eV demonstrate interstitial Zn toms; the PL peaks at 1.5eV denote in-band transitions[12, 13]. Compared to the above two regions, another PL peak at 1.32eV (B1) exists in the first hump of double-hump profile, which represents the Zn-V_{As} complex.

Considering the diffusion and PL results, we may conclude that Zn diffusion mechanism is determined by diffusion sources. Under Ga-rich conditions, Ga vacancies in the surface of wafers were occupied by Ga atoms. Therefore, Zn atoms diffuse by kicking out Ga atoms, as shown in Figure 2.

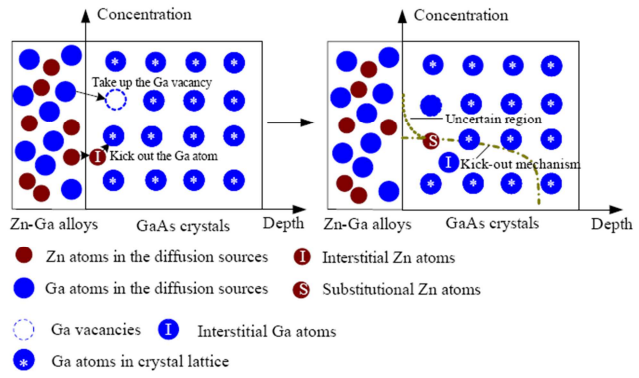


Figure 2. *Schematic diagram of the Zn diffusion under Ga-rich conditions.*

The above diffusion can be described as an interstitial Zn atom (Zn_i^+) kicking out a Ga atom (Ga_{Ga}^0) to the interstitial state (I_{Ga}^+):

$$Zn_i^+ + Ga_{Ga}^0 \rightarrow Zn_{Ga}^-(Zn_s^-) + I_{Ga}^+ + h^+ \quad (1)$$

The function of $D \propto C$ can be got from Equation 1. The simulated $D \propto C$ profile coincides well with the main regions of the single-hump Zn profile, as shown in Figure 1a.

Under pure Zn conditions, Ga vacancies are generated owing to the self-diffusion from the GaAs wafers. Zn atoms would diffuse by taking up the vacancies firstly; therefore the dissociative diffusion would operate in the first hump. This diffusion can be described as an interstitial Zn (Zn_i^+) taking up a Ga vacancy (V_{Ga}^0) and turning to an acceptor (Zn_{Ga}^-):

$$Zn_i^+ + V_{Ga}^0 \rightarrow Zn_{Ga}^-(Zn_s^-) + 2h^+ \quad (2)$$

The function of $D \propto C^2$ can be got from Equation 2, which coincides with the first hump of the double-hump profiles.

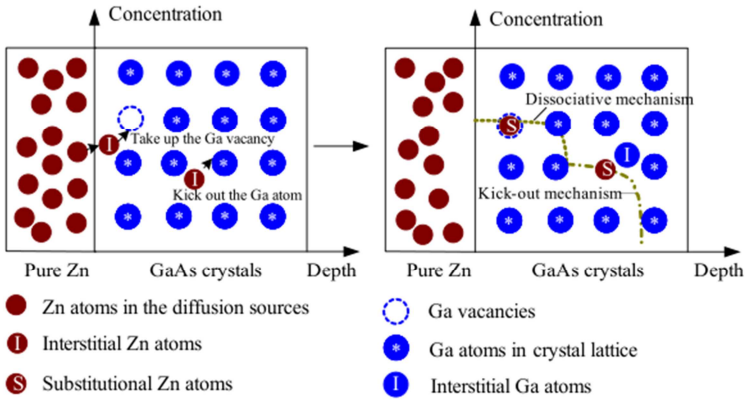


Figure 3. *Schematic diagram of the Zn diffusion under pure Zn conditions.*

The Ga vacancies were generated by self-diffusion; its concentration would decrease to an intrinsic equilibrium value at the frontier of diffusion profile. The short of Ga vacancies would prevent further Zn diffusion. Therefore, the Zn atoms would be compelled to kick the Ga atoms. The overall diffusion process under pure Zn condition is shown in Figure 3.

The diffusion coefficients of double-hump Zn profiles over the temperature range of 525~575°C are listed in Figure 4. It is that the relationship of $D \propto C$ fits for all the tail regions of the double-hump profiles, and the relationship of $D \propto C^2$ fits for the surface region of the double-hump Zn profiles. Arrhenius plot of the surface Zn diffusion coefficients fitted for the tail and surface regions show good linearity, i.e., the distorted phenomenon in double-hump Zn profiles are discovered. This above diffusion model makes a reasonable explanation double-hump profiles and can be used to make accurate predictions under other diffusion conditions.

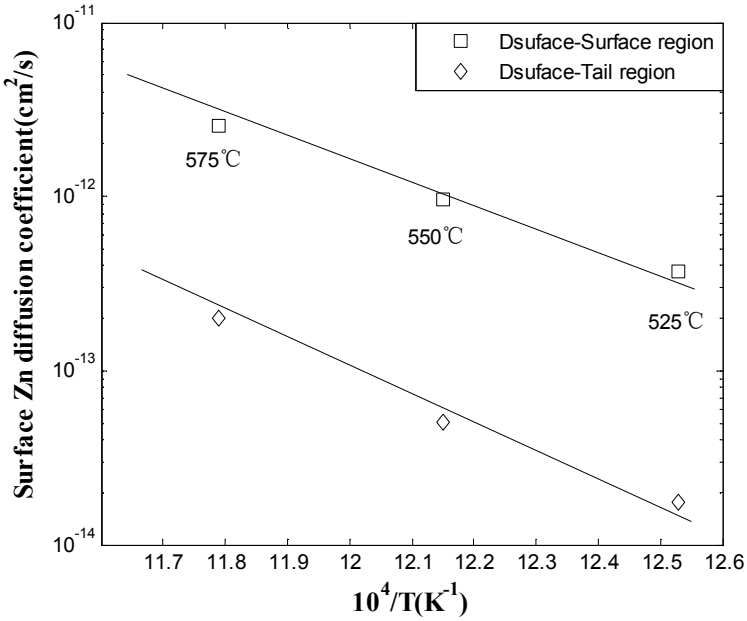


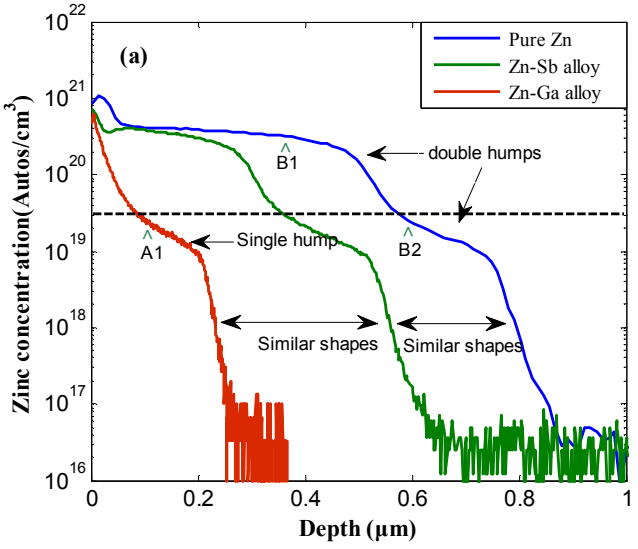
Figure 4. *Arrhenius plot of the surface Zn diffusion coefficients fitted for double-hump Zn profiles.*

In summary, the shape of Zn profile in GaAs is depended by the diffusion source. When Zn-Ga alloy sources are used, the self-diffusion of Ga atoms is hold back, the kick-out mechanism operates owing to short of Ga vacancies, a single-hump profile will be generated. When pure Zn or Zn-As alloy sources are used, Ga vacancies will generate owing to the self-diffusion. Therefore, the dissociative mechanism operates until the concentration of the Ga vacancies reduced to an intrinsic equilibrium value, after which the kick-out mechanism operated. The different relation between D and C for the above two mechanisms causes the distortion of the Zn profile, thus the double-hump profile will be formed.

3.2. Zn Diffusion in GaSb

Zn diffusion in GaSb has been investigated intensively due to the important application in GaSb TPV cells [14-18]. In our previous study, the similar Zn diffusion phenomenon in GaSb have been found as that in GaAs [19]. Recently, several auxiliary experiments have been done to prove the impact of the Ga-self diffusion from matrix atoms. In the following, we will show three groups of diffusion results processed at 500, 550and 610°C.

Figure 5a shows the Zn profiles after diffusion at 500°C for 2h using different sources. Similar to the Zn diffusion in GaAs, the Zn-Sb source can only shorten the first hump. While the Zn-Ga alloy sources can "remove" the first hump dramatically; this result will play a direct role for fabricating of GaSb cells. The first hump should be precisely etched to increase the quantum efficiency of GaSb cells [3, 15], this etching process could be omitted based on the above results. Our PL analyses (Figure 5b) showed that a PL peak located at 0.78eV, which demonstrated the Ga excess existed in the single-hump profile and the second hump of double-hump profile, while this PL peaks didn't exist in the first hump of the double-hump profile. This demonstrates that the Ga atoms have been escaped by self-diffusion under pure Zn or Sb-rich conditions.



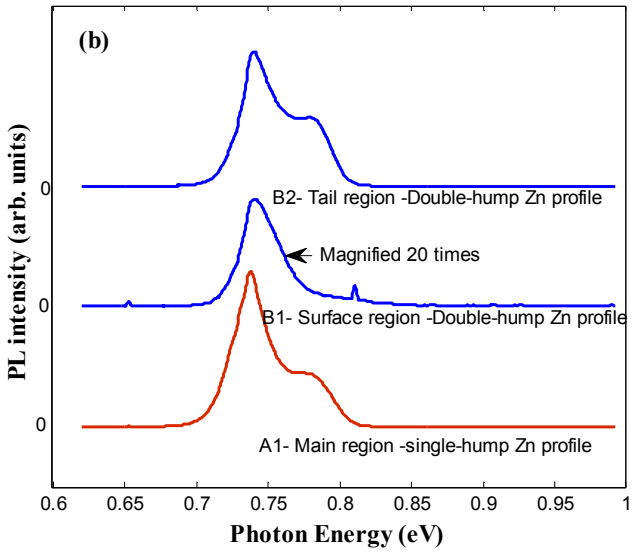
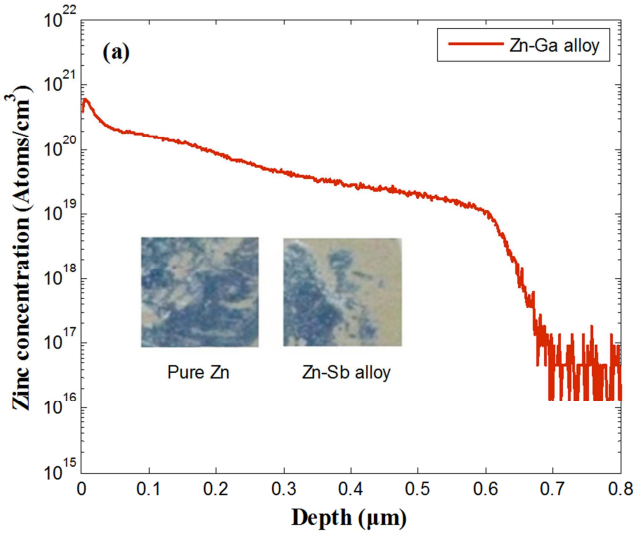


Figure 5. *(a) Zn profiles in n-GaSb under different sources at 500 ℃ for 2h. (b) PL spectra at 15K at the point of A1, B1 and B2.*

Figure 6a shows the diffusion results at 550°C. The GaSb wafer shows a mirrored surface under Ga-rich conditions, and a single-hump profile is obtained. The GaSb wafer shows the blue surface under the pure Zn or Sb-rich conditions. Figure 7 shows the surface morphology and elemental analysis for the blue surface; there weren't other elements on the surface except the Ga and Sb atoms. This may be a "color center" due to component deviation. This "blue-color center" is similar to a "yellow-color center" in ZnO when it is heated in vacuum, which causes the deviation of Zn and O atoms.

Figure 6b shows the diffusion results at 610°C. The wafer after Ga-rich diffusion conditions also shows a mirrored surface and has a single-hump profile inside. While under pure Zn or Sb-rich conditions, the wafers are dissolved due to the escaping of large amounts of Ga atoms.



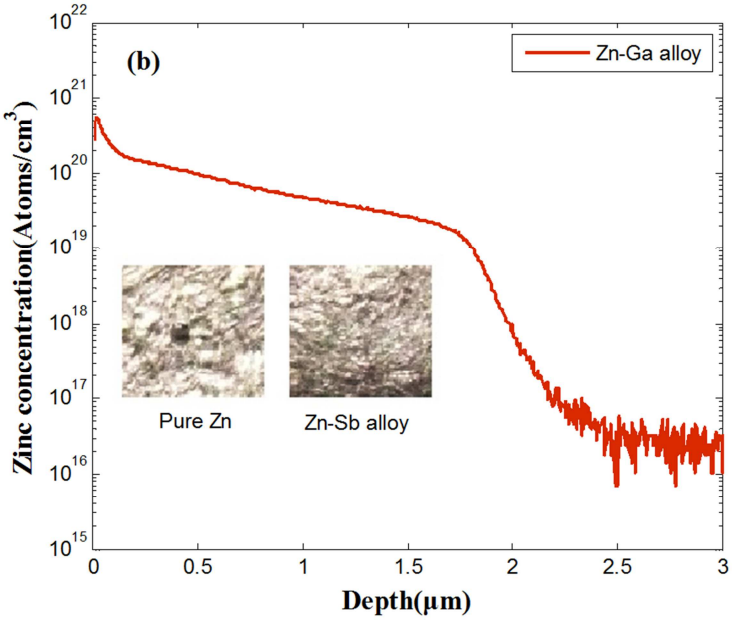


Figure 6. *Zn diffusion results in n-GaSb under different sources. (a)T= 550 ℃, 2h; (b) T=610 ℃, 2h.*

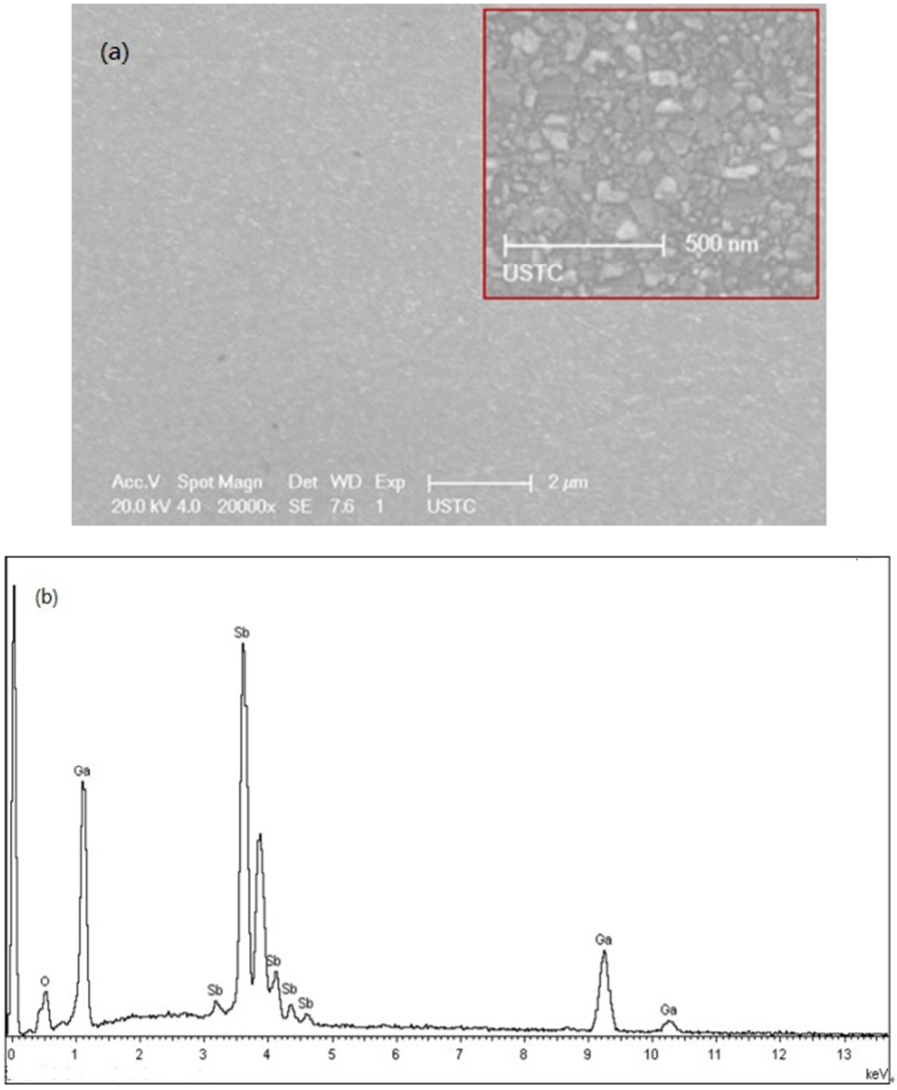


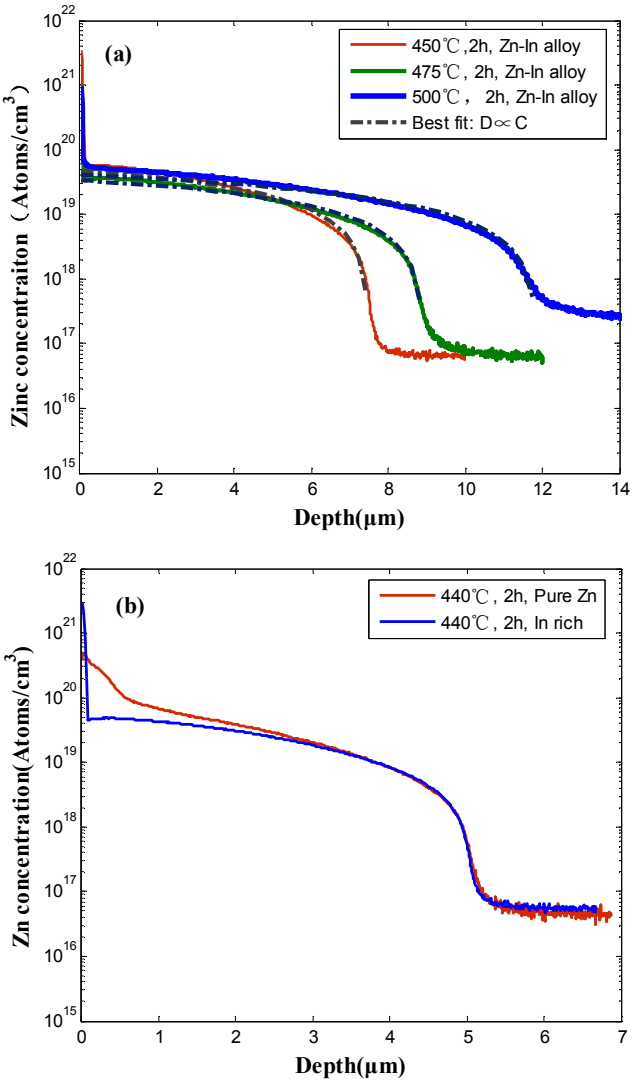
Figure 7. *(a) Surface morphology of the GaSb wafer with the blue surface. (b) Elemental analysis.*

3.3. Zn Diffusion in InAs

The bandgap of InAs is about 0.35eV, the InAs TPV cells fabricated by the Zn diffusion method absorb the photons in the range of 1~3.5 μm [5, 20-23], thus they have import applications in low temperature TPV systems.

Figure 8a shows the Zn profiles in n-InAs under Ga-rich conditions. Over 450~500°C, all InAs wafers show mirrored surfaces and have single-hump profiles inside. The simulated $D \propto C$ profiles fit well for the profiles and the extracted Zn surface diffusion coefficient shows the linearity with the reciprocal of temperature (Figure 8c).

Under pure Zn conditions, the InAs wafer shows the yellow surface above the temperature of 450°C, which demonstrates that the component deviation occurs and produces the "color center". The temperature is decreased to 440°C for comparison, as shown in Figure 8b. Single-hump Zn profiles are obtained under both conditions; this demonstrates that the In atoms can't escape from InAs substrates easily.



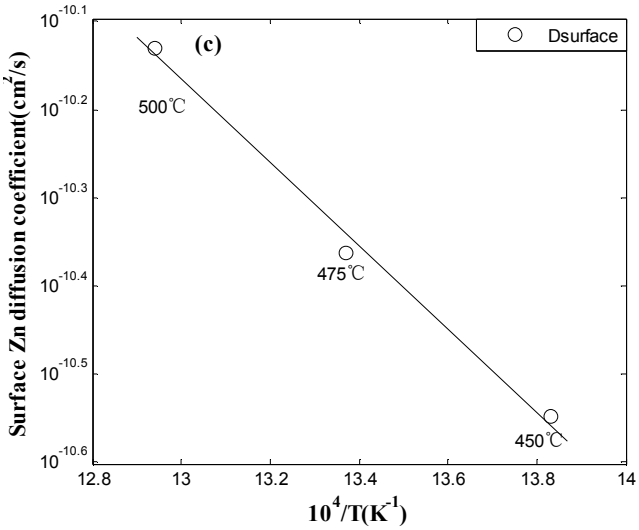


Figure 8. *Zn profiles in InAs under (a)Ga-rich and (b) pure Zn conditions.(c) Arrhenius plot of surface Zn diffusion coefficient fitted for simulating the Zn profiles under Ga-rich conditions.*

4. Conclusion

Different diffusion sources are used to study the diffusion mechanisms of Zn diffusion in III-V compound semiconductors. The III-atoms are crucial to obtain the single-hump Zn profiles; the diffusion results under V-atoms rich conditions are similar to that of pure Zn conditions. Under pure Zn or V-atoms rich conditions, the double-hump profiles will be obtained in GaAs and GaSb. The existing of group III-atoms in diffusion sources would "cut off" the first hump, thus single-hump Zn profiles would be obtained. The In atoms are stable in InAs substrates, thus the single-hump Zn profiles would be obtained under pure Zn or In rich conditions.

Acknowledgements

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