Study of closed-tube Cd diffusion in InSb for mid-IR detector-based applications

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Abstract

Diffusion process of Cadmium (Cd) in indium antimonide (InSb), in a closed tube system, was studied using Hall measurement technique. Various experiments are carried out to achieve a suitable and sustainable procedure. Process details are reported and discussed in the context. Impurity concentration profiles are modeled using an optimized interstitial-substitutional approach. These Mathematical models are in good agreement with experimental data and can be employed in numerical simulations of InSb-based devices.

Keywords: Condensed matter physics, Materials science, Engineering

1. Introduction

Impurity doping is one of main steps in fabrication of opto-electronic devices. Ion implantation and closed (or open) tube diffusion techniques are widely used for impurity doping [1, 2, 3, 4, 5, 6, 7, 8]. Diffusion of impurities can be challenging in some materials and compounds. For example, in III—V compounds, vapor pressure of group V component is usually high. Consequently, a thermal decomposition is possible on the surface. To prevent this, a closed tube system should be used. In closed tube systems, an adequate vapor pressure of the group V element, retains the surface. In this system, two thermal zones with different temperatures are used for substrates and dopants, respectively. Choosing the proper distance between these zones and locating the right...
place for them inside the system is very critical. The weights of the materials (dopants and vapor pressure stabilizers) are also very important. A sealed quartz ampoule is typically used as the closed tube system. Inserting the materials and substrates inside the ampoule and sealing of the ampoule are intricate. The main disadvantage of such systems is their cost. Total expenses for a closed tube diffusion system are usually high compared to a similar process in silicon. Albeit there are difficulties and complications in performing such processes, but with enough care and effort, efficient and acceptable results with minor costs are achievable [1, 2, 3, 4, 5, 6, 7, 8].

In the past decades, much effort has been devoted to analyzing and performing the diffusion of impurities in InSb [1, 2, 3, 4, 5]. However, diffusion of acceptors, such as group II impurities, has received the most attention. Different reports for diffusion of Zinc in InSb with different techniques can be found in literature [1, 2, 3, 4], yet these reports are dissimilar and no sensible accord can be found between them. Diffusion of Cd in InSb [4, 5] and in InP [6] have also been investigated. In diffusion of impurities in InSb, vapor [4] and radioactive [5] sources have been utilized by various researchers. In these studies, impurity profiles are extracted by means of pn junction [4] and autoradiographic sectioning techniques [5], respectively. In other reports for diffusion of Cd in InSb, a specific behavior in impurity profile monitoring has been observed [9, 10]. A sharp front by the junction and a concave area (in logarithmic scale) adjacent to the surface is reported [9, 10]. This unusual behavior in impurity diffusion usually occurs in III–V compounds [11]. Diffusion of zinc in InP [8], InAs [8] and GaAs [11, 12] and also diffusion of phosphorus in GaAs [13] are examples of such behavior. Diffusion of group II acceptors in III–V compounds is investigated using reaction-diffusion equations in ref [14]. In ref [15], Cd diffusion in GaAs has been studied in the temperature range of 756–1201 °C. In this study, diffusion profiles have been extracted using secondary ion mass spectroscopy and spreading-resistance techniques. In ref [16], substitutional and interstitial-substitutional diffusion mechanisms of Zinc in InP are attributed to the flow rate of the impurity source. Numerical modeling for diffusion of Zinc in GaAs is presented in ref [17]. Numerical studies of anomalous fast diffusion in metallic alloys and semiconductors can also be found in ref [18]. Cd doping profiles in InSb, grown by the vertical Bridgman technique, are reported in ref [19]. Reports for self-diffusion of Cd in CdTe (in temperature range of 350–650 °C) can be found in ref [20]. In their study, diffusion profiles are extracted using anodic oxidation sectioning technique. Extrinsic diffusion of Zn in GaSb based on kick-out and dissociative diffusion mechanism, is reported in ref [21]. Modeling of the experimental impurity profiles using continuum theoretical calculations are also reported in ref [21]. Zn diffusion in GaSb is investigated in ref [22] and Kink-and-tail type diffusion profiles are resulted. A substitutional-interstitial-diffusion (SID) mechanism is proposed in ref [23] for diffusion of chromium in GaAs. Further information about diffusion in compound semiconductors can be found in ref [24].
In the present study, Cd is evaporated from a solid source, in a closed tube system. The evaporated Cd fills the ampoule and consequently diffuses into the InSb substrates. After the diffusion process, conventional Hall measurements were carried out to extract the impurity concentration profiles, and will be presented in next sections.

2. Experimental

Diffusion processes, which are henceforth reported, are employed in fabrication of InSb-based array and single-element infrared detectors. Impurity concentration profiles and mathematical models for these diffusions will be discussed in next sections.

Cd acceptors are used as impurities in theses diffusion processes. One of the main factors in choosing the dopant material is its diffusibility. Cd is a slow diffusing material. As a result, diffusion process can be well-controlled. A two-zone system with different temperatures in each zone is utilized for diffusion of Cd. Temperatures of InSb substrates and Cd dopants are defined separately using these zones. Schematic of the closed tube quartz ampoule is illustrated in Figs. 1 and 2. It’s obvious in these figures that InSb substrates are devised in the middle (With a distance of 30 cm from bottom of the ampoule, as shown in Fig. 3). Cd dopants are placed in the bottom, in a spoon shaped holder. Another holder is embedded for small InSb pieces. Geometrical properties of the ampoule are shown in Fig. 3.

After preparing the closed tube system, InSb substrates should be cleaned carefully, before being inserted inside the ampoule. It’s noteworthy that 2"', n-type InSb wafers with (111) crystal orientation are used in these experiments. Impurity concentration of wafers were $5e14 \text{ cm}^{-3}$ at 77 K with etch pit densities of less than 100 cm$^{-2}$. The wafers have two faces, namely, Sb-face and In-face. In this work, only Sb-faces of the wafers have been used. The cleaning process of the wafers is as follows:

![Fig. 1. Schematic of the closed tube ampoule used in diffusion processes.](https://doi.org/10.1016/j.heliyon.2018.e00593)
Organic cleaning:

a. Acetone + alcohol \((t = 5\) minutes \(- T < \) boiling point of the solvents-repeat the process for 3 times) 

b. Rinsing in DI water 

Cleaning of the minerals:

a. \(\text{HNO}_3:CH_3\text{CooH}:\text{HF}:\text{H}_2\text{O} (2:1:1:10)\) \((t = 1\) minute \(- T = \) room temperature) 

b. Rinsing in DI water \((t = 5\) minutes \(- T = \) room temperature) 

c. Rinsing in DI water \((t = 5\) minutes \(- T = 80^\circ\)C) 

d. Rinsing in DI water \((t = 5\) minutes \(- T = \) room temperature) 

e. Dehydrating with \(\text{N}_2\) 

Since the diffusion is performed in a closed tube ampoule, the ampoule and all of its contents should be cleaned with care. Cleaning procedure for the ampoule and its contents is as follows:

a. Immersing in lotion \((\text{H}_2\text{SO}_4 (2.5\) lit) + \text{K}_2\text{Cr}_2\text{O}_7 (70\)gr\)) for 2 hours.
b. Rinsing in DI water for 15 minutes in room temperature
c. Rinsing in DI water for 15 minutes - $T = 80^\circ C$
d. Immersing in $\text{HNO}_3 + \text{HCl} (1:3)$ for 15 hours
e. Rinsing in DI water for 15 minutes - $T = 80^\circ C$
f. Baking in oven for 2.5 hr - $T = 140^\circ C$

After cleaning the wafers and the ampoule, Cd balls (which act as the impurity sources) should be cleaned. The cleaning instruction is as follows:

a. Immersing in alcohol for 5 minutes (in room temperature)
b. Adding HNO$_3$ and shaking for 2 minutes in room temperature
c. Cleaning with alcohol

Small InSb pieces which act as the Sb vapor pressure stabilizer, should be cleaned in a way similar to the wafers. In the closed tube system of diffusion, Cd vapor fills the ampoule. The vapor then diffuses into the heated substrates. However, this process is not as easy as it may seem. Sb atoms tend to separate from the surface of the wafer. If this happens, the wafer surface would be In-rich which will lead to an In:Cd alloy on the surface. An example of such an alloy which has been occurred in one of the experiments is shown in Fig. 4a. To prevent this from happening, small InSb pieces are devised inside the ampoule. These pieces stabilize the vapor pressure of the Sb inside the ampoule (mentioned in Fig. 2).

The amount of these pieces should be reasonable. If more than enough pieces are used, another kind of alloy would occur which is because of abundance of Sb atoms on the wafer. Proper choice of weight for these pieces is experimentally estimated to be 2.4 gr.

Amount of Cd balls are also very important. An inappropriate choice in this case, would lead to Cd pile-up on the surface (Fig. 4b). Experimental results show that a convenient weight for Cd balls should be in the range of 360–390 mgr.

![Fig. 4. Optical microscope images of a) an In-rich surface in result of separation of Sb atoms from the surface and b) Cd-rich surface because of abundance of Cd on the wafer.](https://doi.org/10.1016/j.heliyon.2018.e00593)
Geometrical properties of the holders are shown in Figs. 5 and 6. After cleaning of the ampoule, holders, wafers, Cd balls and InSb pieces, the diffusion process can be carried out. To start the diffusion process, wafers, Cd balls and InSb pieces should be placed inside the ampoule. Two or four dummy silicon wafers are placed in front and back of the InSb wafers to regulate the Cd vapor flux around the InSb wafers. The ampoule is then vacuumed to the pressure of $3 \times 10^{-6}$ Pa. Thereafter, the ampoule is sealed and is inserted inside the diffusion furnace.

As mentioned before, in diffusion furnace, two temperature zones are defined for Cd balls and InSb wafers, separately. In this work two conditions are investigated, which are shown in Table 1.

After executing the diffusion process, two main facts should be considered in evaluating the quality of the process. First, surface of the wafers should be physically acceptable. So that, no alloys should be present on the surface. Second, IV curves of the desired structure should be extracted and analyzed. In the next sections, theory...
of the diffusion, diffusion results, mathematical models and intended infrared detectors are discussed.

3. Theory

Diffusion of atoms in solids can be efficiently described with Fick’s first and second laws. Particle current density and particle concentration flow rate can be defined with equations 1 and 2 (in 1D case).

\[ s = -D \frac{\partial C}{\partial x} \]  
\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \]  

With

\( s \) = particle current density  
\( C \) = particle concentration  
\( D \) = diffusion coefficient  
\( x \) = direction perpendicular to the surface through which the particles enter the solid  
\( t \) = time.

Assuming that diffusion coefficient is independent of concentration of impurities and consequently, independent of \( x \), equation (2) simplifies to equation (3).

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

In the case of a constant impurity source on the surface, equations (1) and (2) will result in a complementary error function for the spatial distribution of the diffusing atoms. Equation (4) shows this result.

\[ C(x) = C_{surf} \text{erfc} \left( x/2\sqrt{Dt} \right) \]  

With \( C_{surf} \) defined as equation (5):
\[ C_{\text{surf}} = C_{\text{sou}} \frac{k \theta}{k + \theta} \quad (5) \]

and \( C_{\text{sou}} \) = atom concentration in the source; \( K \) = distribution coefficient; \( \theta = D_{\text{sou}}/D \); \( D_{\text{sou}} \) = diffusion coefficient in the source. Equation (6) defines the diffusion length.

\[ 2\sqrt{Dt} = L_D \quad (6) \]

Where \( L_D \) is the diffusion length.

In III–V compounds, especially at high dopant concentrations, a sharper front results from the diffusion process which is not expected from equation (5) [24]. Such impurity distributions cannot be analyzed with a constant diffusion coefficient. In the next section the modeling procedure for such profiles will be discussed.

4. Model

Following the discussed diffusion processes, here, results on impurity concentration profiles are reported. Modeling procedure will also be explained. Beginning with experiment 1 of Table 1, the concentration profile of the diffusion for this experiment is shown in Fig. 7. To extract this profile, standard Hall measurements is used. The SIMS method can also be used for profiling [25, 26]. To do the Hall measurements, 1 cm \( \times \) 1 cm diffused samples are used. Points in Fig. 7 are results of these measurements. The concentration vs. distant from the surface (in \( \mu m \)) is illustrated in Fig. 7. For each point in the graph, an etching step is carried out on the sample. The solution of \( \text{Citric (50)} + \text{H}_2\text{O}_2 \) (1) is used to etch the samples. Afterwards, concentration of the samples is measured.

Impurity profile for experiment 2 of Table 1 is depicted in Fig. 8. It is noteworthy that experiments 1 and 2 are for array and single-element photo-detectors, respectively.
With a background concentration of $5 \times 10^{14}$ at the temperature of 77 K, junction depth ($x_j$) for experiments 1 and 2 are 0.95 $\mu$m and 3.4 $\mu$m respectively.

As mentioned earlier, diffusion coefficient in III–V compounds is not constant. Figs. 7 and 8 confirm this fact. To include such behaviors, the so called interstitial–substitutional model [27] is employed in modeling of the impurity profiles. Equation (7) describes this model.

$$D = \frac{D_c}{(1 + K \exp(-x/L))} \quad (7)$$

$$D_c = D_0 \times \frac{D_i}{C} \quad C > D_i$$

$$D_c = D_0 \frac{C}{D_i} \quad C \leq D_i$$

With $D_0$, $K$, $L$ and $D_i$ being constant. $x$ and $C$ are distance from the surface and concentration, respectively. Constants in equation (7) are calculated for experiments 1 and 2 and also are shown in Table 2.

With diffusion coefficients in hand, impurity concentration profiles can be modeled using the well-known erfc model. Equation (8) shows this model.

$$C = C_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (8)$$

**Table 2. Constants in equation (6) for experiments 1 and 2.**

|                  | Experiment 1     | Experiment 2     |
|------------------|------------------|------------------|
| $D_0$            | $3.8 \times 10^{-13}$ | $3 \times 10^{-12}$ |
| $K$              | 33               | 20               |
| $L$              | $0.95 \times 10^{-6}$ | $1 \times 10^{-5}$ |
| $D_t$            | $5.5 \times 10^{18}$ | $3.7 \times 10^{17}$ |
With $C_0, x, D$ and $t$ being the initial concentration, distance from surface, diffusion coefficient and diffusion time. The results for diffusion coefficients and also diffusion profiles for experiments 1 and 2 are shown in Figs. 9, 10, 11, and 12. An increase-maximum-decrease behavior is obvious in Figs. 9 and 11 for the diffusion constants. Impurity profiles are modeled using these diffusion constants. Impurity models are plotted in Figs. 10 and 12. It can be seen that there is a good agreement between experimental data and mathematical models.

Proposed models can be used in numerical simulations of InSb based detectors. Albeit there are other models proposed in the literature, but a specific diffusion model for this work was necessary. Moreover, in other reported experiments [27, 28, 29], details of diffusion processes are not included. Therefore, this work has some valuable and detailed information about the diffusion process of Cd in InSb which has not been reported elsewhere.

![Fig. 9. Calculated Diffusion coefficient for experiment 1.](image)

![Fig. 10. Experimental data (green squares) and calculated model (red line) of concentration vs. distance from the surface for experiment 1 of Table 1.](image)
Hereafter, a brief introduction about two types of infrared detectors, for which diffusion processes are carried out, is presented. Diffusion number 1 is for a focal plane array detector which operates at the spectral range of 3.7–4.8 μm. In this case, light enters from the back side of the photodiodes. A schematic view of this case is shown in Fig. 13.

As it can be seen in this figure, a pn photodiode which is passivated with two layers of anode oxide and SiO, is attached to a readout circuit (ROIC) pixel, using the indium bump (or so called flip chip) technique. It should be emphasized that this schematic only shows a single pixel and not the whole array (which is a matrix of 320 × 256 of these photodiodes). Since the p side of the detector is connected to the ROIC, light enters the structure from the n side. Because of that, a shallow junction in the p side would be sufficient to collect the optical carriers. It’s notable that the thickness of the n side of the photodiode is reduced to about 15 μm (by means of mechanical
polishing followed by a chemical etching step). The final thickness of the $n$ side is in proportion to the efficient light absorption depth which will lead to an appropriate responsivity.

Diffusion number 2 is for a single element photo-detector with the same operating spectral range (but with a different structure from the previous one). In this case, the IR radiation enters the structure from the top surface ($p$ side). Metal contacts are indium solders (no lithography is used for metals). Because of that, a $p^+$ surface is needed to have an ohmic contact on the surface. A deeper diffusion profile is used in this case to keep the $p^+$ under the metal. Other parts of the sensitive area are etched.
chemically for maximizing the absorption in the $p$ layer. The cross section of this photodiode is shown in Fig. 14.

5. Conclusion

In this paper, the detailed procedures, necessary for diffusion of Cd in InSb, for fabrication of InSb-based single and array mid-IR detectors, are reported. Process details such as the weights of Cd balls or InSb pieces and also the geometrical properties of the closed tube ampoule and holders, which are results of various experiments, are discussed. The impurity concentration profiles for two diffusion processes are extracted using standard Hall measurements. Mathematical models for the extracted profiles are proposed by means of an optimized interstitial-substitutional approach. Proposed models can be used in numerical simulations of InSb based infrared detectors.

Declarations

Author contribution statement

E. Pourali and A. Erfanian: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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