Substrate Orientation Dependence of Fe Doping in MOVPE-Grown InP

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We studied the substrate orientation dependence of Fe doping in InP grown by MOVPE. We have found that both the incorporation efficiency and saturation concentration of electrically active Fe depend strongly on the substrate orientation for the first time. The saturation concentration exceeds $1 \times 10^{18}$ cm$^{-3}$ on A-face substrates, in contrast to about $6 \times 10^{16}$ cm$^{-3}$ on (100). We propose a model that explains the saturation mechanism and its substrate orientation dependence.

1. Introduction

Fe-doped semi-insulating InP is widely used as a burying layer in InGaAsP/InP buried heterostructure (BH) laser diodes, because it reduces both leakage current and parasitic capacitance. From the view of current confinement, semi-insulating property of a burying layer, which is grown on different orientations from (100), plays an important role. However, Fe doping has been studied using only the (100) substrate thus far.

In this work, we report the substrate orientation dependence of Fe doping in InP grown by MOVPE.

2. Experiment

Fe-doped InP layers were grown at 600°C and 76 Torr by low-pressure MOVPE using ferrocene (Cp2Fe) as a doping source. TMI and PH3 were used as source gases and SiH4 for n-type doping. The V/III ratio was 120 and the growth rate 3 μm/hr. We used Sn-doped InP substrates with orientations of (100), (811)A, (511)A, (311)A/B, (211)A/B, (111)A offset 5° toward (011), (111)B offset 5° toward (011), (011) offset 5° toward (111)A/B, and (011) offset 15° toward (111)A/B. The growth rate on these substrates was the same within measurement accuracy.

We determined the concentration of electrically-active Fe from the compensated n-type impurity concentration in an Fe- and Si-codoped layer. The n-type impurity concentration was measured by C-V carrier concentration profiling (Polaron). The atomic concentration of Fe was measured by SIMS. To determine the semi-insulating property, we evaluated the current-voltage characteristics of mesa-shaped n-i-n diodes.

3. Results

Figure 1 shows the ferrocene flow rate dependence of the electrically-active Fe concentration for various orientation substrates. At low flow rates, the active Fe concentration is proportional to the ferrocene flow rate. We confirmed that the active Fe concentration agrees with the Fe atomic concentration. At higher flow rates, the active Fe concentration saturates except at (211)A and (311)A, although the Fe atomic concentration does not saturate. We could not determine the saturation concentration on (211)A and (311)A because Si doping exceeding $1 \times 10^{18}$ cm$^{-3}$ damaged the surface morphology. Both Fe incorporation efficiency and the saturation concentration of electrically active Fe depend strongly on substrate orientation. We plotted these two parameters as a function of the substrate orientation in Fig. 2. Incorporation efficiency, determined from the non-saturated region and normalized to that of (100), peaked at (311)A/B and was lowest at (111)B. The saturation concentration increased with the offset angle toward (111)A/B from (100). On A-face substrates between the (311)A and (011) orientation, the saturation concentration exceeded $1 \times 10^{18}$ cm$^{-3}$. On B-face substrates, the saturation concentration was about $6 \times 10^{16}$ cm$^{-3}$, nearly equal to that on (100). This dependence of Fe saturation concentration is significant, contradicting the previous idea that the saturation concentration is limited by Fe solubility in InP. If saturation is caused by the solubility limit, the saturation concentration should be independent of the substrate orientation.

To study the semi-insulating property of Fe-doped layers grown on various orientations, we evaluated the current-voltage characteristics of mesa-shaped n-i-n
diodes fabricated on (100), (311)A/B, (111)B offset 5° toward (100), and (011) offset 5° toward (111)B. The thickness of Fe-doped layer is 2 μm and the ferrocene flow rate was fixed at 20 ccm. This flow rate is just under the saturation point on (100) and typical for actual burying growth. 3) Fig. 3 shows the current-voltage and the differential resistivity-voltage characteristics. Resistivity in the ohmic region was lowest at 5.0x10⁷ Ω-cm on (111)B, in contrast to 2.0x10⁸ Ω-cm on (100), due to the low Fe incorporation and high background impurity level on (111)B. Resistivity around 1 V exceeded 1x10¹⁰ Ω-cm on (311)A, perhaps reflecting the high concentration of active Fe. Critical voltage V_cr of rapid current increase by trap-filling is theoretically proportional to the unoccupied deep-level concentration 5). V_cr on (100), (311)B and (011) were nearly equal, reflecting nearly equal concentrations of active Fe on these substrates. V_cr was highest on (311)A. Because saturation occurred on (311)B at this ferrocene flow rate, this result shows that the active Fe concentration on (311)A is higher than the saturation concentration on (311)B.

4. Discussion

4-1. Incorporation efficiency

We consider Fe incorporation process as shown in fig. 4. Because the ferrocene decomposition is considered to be incomplete at our growth temperature, 5) Fe is supplied as atoms or molecules. Incorporation of low-volatile impurity was considered to depend weakly on orientation if the impurity is supplied as atoms. 6) Since Fe has low volatility and its incorporation depends strongly on orientation, Fe should be supplied mainly as molecules. Considering that low-volatile Fe atoms are difficult to desorb from the surface, the Fe incorporation efficiency is governed by the adsorption and decomposition of partly decomposed ferrocene molecules on the surface. Decomposed Fe atom may migrate on the surface and be incorporated at stable sites.

Zn incorporation in AlGaInP is high on (311)A, 6) as Fe in InP. Because the (311) surface has the highest step density, Zn atom is considered to be preferentially adsorbed at steps on A-face substrates. Since Fe incorporation is high on (311)A/B, we consider that partly decomposed Fe molecules are preferentially adsorbed and/or decomposed at steps or kinks on the surface between (100) and (111)A/B orientations.

4-2. Saturation concentration

We consider saturation to be caused by FeP precipitates forming. Fe atoms over the saturation concentration are known to exist as FeP precipitates in InP layers grown on (100). 7) Since the saturation concentration depends on orientation, the precipitation should occur on the growth surface. The growth of FeP precipitates should be limited by the supply of Fe atoms which migrate on a surface, because they grow in a P-rich atmosphere. When the concentration of Fe migrating on a surface exceeds the critical value, precipitates may begin to form. The precipitation formation should prevent the number of Fe atoms incorporated into group-III sites from increasing, and cause saturation.

Assuming that the migration of Fe atoms and the precipitation formation depend on the substrate orientation, we considered why the saturation concentration is high on A-face substrates. Fig. 5 shows the surface atomic structure on (100) tilted toward (a) (111)A and (b) (111)B. The surface is assumed to be covered with P atoms and surface reconstruction is neglected. Unlike a (100) terrace which provides group-III sites with two dangling bonds from P atoms, the A-face step provides group-III sites with three dangling bonds. Group-III site with three dangling bonds may capture Fe atoms more strongly than that with two dangling bonds. 8) We believe that this strong capture mechanism reduces the migration of Fe atoms and cuts down the FeP precipitation formation. The density of this strong capture site increases with the offset angle toward (111)A from (100) and is high on A-face substrates, so we consider that the saturation concentration increases with the offset angle toward (111)A from (100) and is high on A-face substrates. In contrast, the B-face step, like the (100) terrace, provides group-III sites with two dangling bonds. B-face substrates between (100) and (111)B do not provide strong capture sites except at low-density kinks. So we assume that precipitates form easily and the saturation concentration is low on B-face substrates.

5. Conclusion

We investigated the substrate orientation dependence of Fe doping in InP grown by MOVPE. The incorporation efficiency has the peaks on (311)A/B and is lowest on (111)B. We consider that the incorporation efficiency is governed by the adsorption and decomposition property of partly decomposed ferrocene molecules on the surface. The saturation concentration exceeds 1x10¹⁸ cm⁻³ on A-face substrates, but is about 6x10¹⁶ cm⁻³ on (100) and B-face substrates. We proposed a model that explains the saturation mechanism and why saturation concentration depends on substrate orientation.

References


Fig. 1 Ferrocene flow rate dependence of electrically-active Fe concentration for various orientation substrates.

Fig. 2 Normalized Fe incorporation efficiency and saturation concentration of electrically active Fe as a function of substrate orientation. The dashed line indicates that saturation concentration on (311)A and (211)A substrates are even higher.

Fig. 3 Current-voltage and differential resistivity-voltage characteristics of mesa-shaped n-i-n diodes.

Fig. 4 Fe incorporation process.

Fig. 5 Surface atomic structure of steps on (100) tilted toward (a) (111)A and (b) toward (111)B.