Residual impurities and electrical properties of undoped LEC InAs single crystals

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Abstract: Impurities and their influence on the properties of InAs single crystals have been studied by combining the results of glow discharge mass spectrometry (GDMS), Hall measurements, Raman scattering and infrared absorption. The results indicate that carbon is a major impurity in LEC-InAs single crystals and exhibits a significant influence on the electrical and optical properties.

Key words: InAs; single crystal; impurity; defect
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1. Introduction

InAs is a direct band-gap compound semiconductor with a band-gap of 0.36 eV (300 K). InAs single crystals are used as substrates for growing heterojunction superlattice materials such as InAsSb, InAsPSb, InNAsSb, and AlGaSb, which are widely used in the production of 2–14 μm wavelength infrared light-emitting devices[1−4] and quantum cascade lasers[5, 6]. These infrared devices have a bright application prospect in gas monitoring, low-loss optical fiber communications and other fields. In addition, InAs single crystal is an ideal material for new type heterojunction devices[7], THz wave generation[8] and infrared windows. With the continuously improving performance of the devices, demand for quality and purity of the substrate is urgent. Thus, it is necessary to study the formation mechanism of the defects, the properties of the impurities and control of the growth process to obtain high-quality InAs single crystals.

At present, the liquid encapsulated Czochralski (LEC) method is generally used in InAs single crystal growth. It has been proved that non-doped InAs single crystals grown by using raw materials with more than 6N's purity turns out to be N-type with a free-electron concentration up to 3×10^{16} cm^{-3}. There are few reported research results on residual impurities and native defects in InAs single crystal. Correspondingly, the origin and formation mechanism of impurities and defects are still not clear.

In this paper, high sensitivity glow discharge mass spectrometry (GDMS) was used to analyze the residual impurities of undoped LEC-InAs single crystal, quantitatively. A study of the origin of donor impurities and defects and their influence on the nature of the material is made by combining Hall measurements, Raman scattering and infrared absorption. An approach to impurity control is explored based on the results.

2. Experiment

InAs single crystals are grown by two different LEC growth processes for comparative purposes. One process is to carry out InAs single crystal growth directly after *in-situ* synthesis (named process A). The other is to pre-synthesize poly-InAs, and then LEC crystal growth proceeded by melting the polycrystalline material (named process B). Synthesis of the polycrystalline InAs was conducted in a high-pressure crystal furnace. Elements In and As with 6N–7N's purity, together with 300–400 g dehydrated B_2O_3, were added to a quartz crucible and then synthesized in a high-pressure furnace. It is believed that process A causes more contamination than process B in the growth process. Growth orientation of the InAs single crystal is (100) or (111)[9].

The sample for GDMS analysis is a rod shaped single crystal InAs with a size of 20 × 2 × 2 mm^3. Acetone, anhydrous ethanol, deionized water ultrasonic cleaning and acid etching were applied to remove the surface contamination prior to the measurement by V9000-type GDMS spectrometer in Shanghai Institute of Ceramics, CAS. In addition, conventional Hall measurements, Raman scattering and infrared absorption analysis were also used to study electrical properties and defects in the samples.

3. Results and discussions

Table 1 shows the Hall measurement results of the two types of InAs single-crystal samples. One can see that the mobility of the A-type sample is higher than that of the B-type sample and its carrier concentration is generally lower than that of the B-type sample. It is well-known that the magnitude of carrier concentration and mobility directly reflect impurity content and electrical compensation in semiconductor materials. This result implies a stronger electrical compensation and scattering from a higher impurity concentration in sample B.

In order to further investigate the properties and impurities in the InAs single crystal sample, we carried out GDMS measurement. Typical results of the two types of undoped InAs single-crystal samples are shown in Table 2. From Table 2, we can see that the concentrations of C, N, O are apparently higher than other impurities in the non-doped InAs single crystal. In addition, sample B has a much higher concentration of C, N and O. It also has a relatively higher concentration of silicon,

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Table 1. Room temperature Hall result of the two types of InAs single crystals.

Sample	Purity	Process	Mobility (10^4 $cm^2/(V\cdot s)$)	Carrier concentration (10^{16} cm^{-3})
A	6N–7N	*In-situ* synthesis and signal crystal growth	2–2.5	1.5–2.046
B	6N–7N	Single crystal growth after synthesis of the polycrystal	1.6–2.2	2.8–5.2

Table 2. Typical GDMS results of the two undoped LEC-InAs single crystal samples (ppm, wt).

Sample A				Sample B			
Element	Content	Element	Content	Element	Content	Element	Content
B	0.03	K	0.02	B	0.032	K	0.017
C	23	Ca	0.01	C	173	Ca	0.01
N	0.64	Mn	0.001	N	84	Mn	0.004
O	10	Fe	0.02	O	398	Fe	0.05
Mg	0.004	Cu	0.005	Mg	0.006	Cu	0.052
Al	0.002	Zn	0.01	Al	0.005	Zn	0.08
Si	0.01	Cd	0.02	Si	1.30	Cd	0.04
Te	0.006	Sn	0.02	Te	0.23	Sn	0.031
Cl	0.002	P	1.6	Cl	0.17	P	0.06
Sb	0.005	S	0.24	Sb	0.011	S	0.33

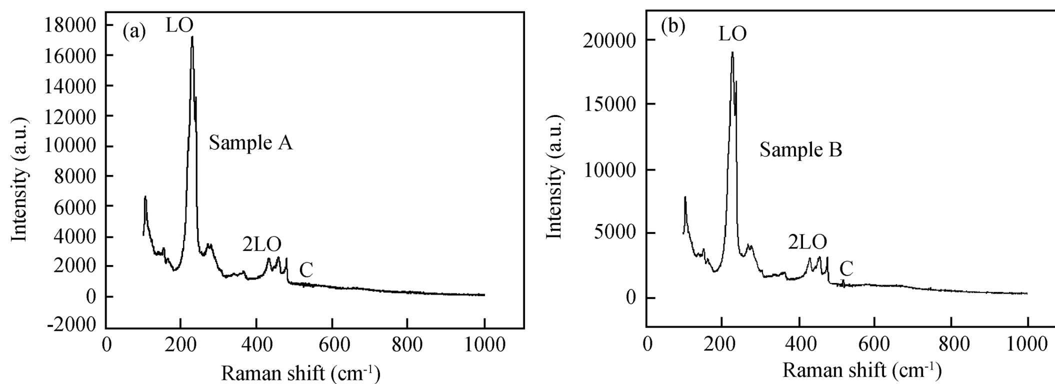

Fig. 1. Raman scattering spectroscopy of the two types of undoped InAs single-crystal samples.

which is most likely contaminated by the quartz crucible used in the preparation process.

Among these impurities, S, Sn, Si, Te act as donors, while Zn, Cd, Mn, etc. act as acceptors. As for the P impurity, it does not affect the electrical properties of InAs single crystal since it is an isoelectronic impurity. The existence of donor impurities in InAs single crystal increases the free electron concentration, but the existence of acceptor impurities results in electrical compensation, reducing the mobility of InAs single crystal. From the order of magnitude of the impurity content, the impurity concentration is substantially consistent with that of free electrons obtained by Hall measurement. Generally, Pb, Fe, Cu, Zn, Cd, Al, Sn, Mg, Ca, C and S come from the raw materials In and As, respectively, according to the reported distribution result for the residual impurity[10]. It is noteworthy that the concentration of C is very high, and meanwhile it is necessary to note that C has been proved to act as a shallow donor in InAs single crystal while in GaAs single crystal it usually acts as a shallow acceptor[11,12]. Therefore, the presence of carbon is bound to increase the conductivity of N-type InAs single crystal. Although there may be signal interference in GDMS while measuring carbon, carbon is basically thought to be an impurity with the highest content in InAs single crystal. The concentrations of donors S, Te, Si, Sn are very low, thus, they are all ruled out as the dominant donor. In addition to the source of elemental arsenic, carbon also most likely comes from the graphite heater and insulation materials during the growth process. The mechanism of carbon incorporation in InAs is possibly similar to that in LEC-GaAs single crystal[13].

It is clear and reasonable that the A-type InAs single crystal is grown in a process with less impurity contamination and has a higher purity. In contrast, the B-type InAs single crystal has a higher impurity content originating from the two step process of polycrystalline synthesis and crystal growth. Therefore, in order to reduce the residual impurity concentration of InAs single crystal, growth conditions and the C content in the raw material must be controlled.

We also carried out Raman scattering measurements to check the influence of carbon in the two types of undoped InAs single crystals, and the result is shown in Fig. 1. In addition to the inherent crystal InAs acoustic phonon scattering, a weak scattering peak was observed at 527 cm^{-1}. This scattering peak has been proved to be C related in InAs[12]. It is noted that the intensity of the C related peak in sample B is apparently

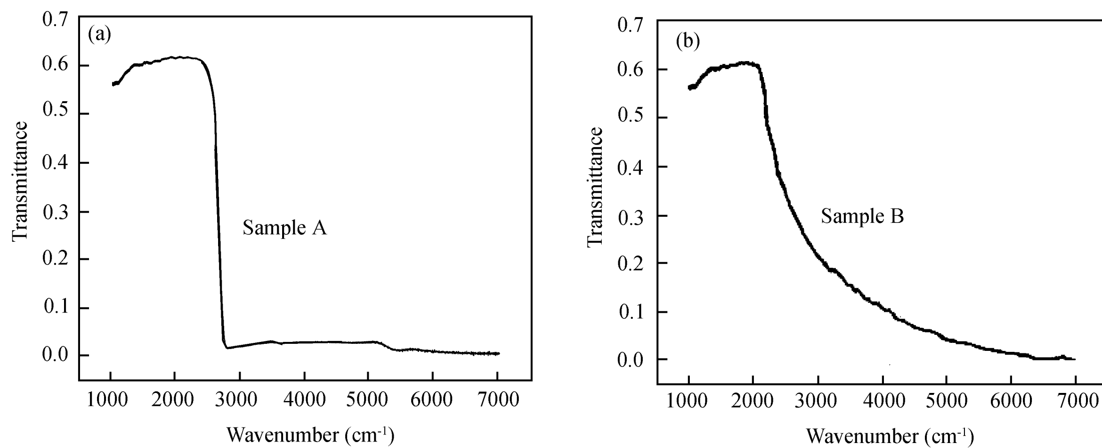

Fig. 2. Infrared transmittance of a high quality undoped LEC-InAs single crystal.

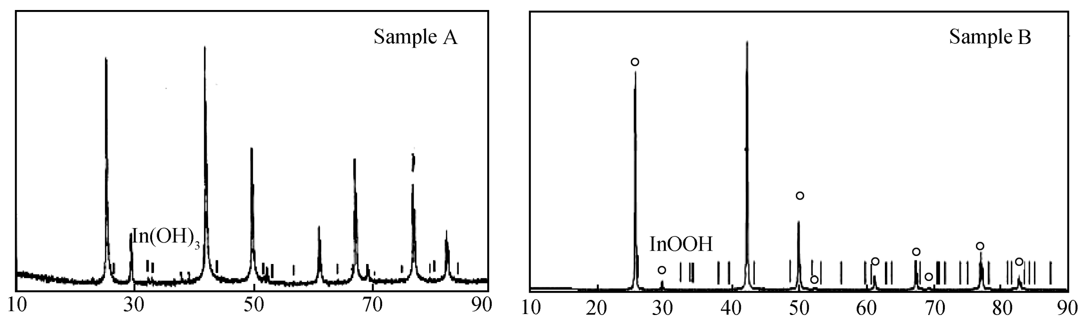

Fig. 3. X-ray powder diffraction of the two types of undoped InAs single-crystal samples.

stronger, suggesting the existence of a higher concentration of C, which coincides with the GDMS results.

Figure 2 shows the infrared transmission spectrum of the two types of undoped InAs single-crystal samples. In the picture of sample B, the band-edge absorption changes slowly from 2100 to 4000 cm^{-1}. Compared with sample B, we can see clearly that the cutoff wavelength of band-edge absorption of sample A changes steeply, indicating there is no obvious light absorption caused by impurities and defects, implying good crystallization quality and high single crystal purity.

Hydrogen is a very popular residual impurity in semiconductor materials. Since it is difficult to accurately measure H by GDMS mass spectrometry, we analyze the two types of undoped polycrystalline InAs samples with X-ray diffraction phase analysis (XRD) in order to determine whether there are O, H impurities in the material. Under high-resolution XRD test conditions, the existence of $In(OH)_3$ in InAs single crystal is detected, indicating that InAs single crystal contains a higher concentration of O and H. A typical result is shown in Fig. 3. The impact of H and O on InAs single crystal is still unclear. However, H and C that occupy the site of arsenic in InAs single crystal can form complex defects, and act as acceptors[14].

Combining all these results, it can be considered that carbon has a significant impact on the electrical properties of InAs single crystal. Thus carbon concentration in raw material arsenic must be controlled in order to reduce the carbon content of InAs single crystal. In addition, since carbon is most likely incorporated in LEC-InAs single crystal through the melt in the diffusion of CO that is supplied by the reaction of residual water in B_2O_3 with carbon in the graphite heater, a process similar to the LEC-GaAs single crystal[14]. Therefore, it is necessary to control the water content of B_2O_3 strictly. In the two-step process, the increase of the amount of carbon contamination is believed to be a result of the longer duration of the reaction during the growth process, thereby increasing the concentration of InAs single crystal.

4. Conclusion

Carbon is a main donor impurity of LEC-InAs single crystal and has a critical influence on its electrical properties. The carbon content in arsenic as well as the water content in B_2O_3 must be controlled in order to reduce the carbon concentration in InAs single crystal. High-pressure *in-situ* direct synthesis with LEC single crystal growth is an effective approach to suppress the contamination of the impurity and prepare high-quality, high purity InAs single crystal.

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