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Impurity band conduction in Mn-doped p type InAs single crystal

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1. Introduction

Ⅲ-Ⅴ compound semiconductors doping with Mn are attracting an increasing interest not only for potential spintronics applications [1–[3\]](#page--1-0) but also for favorable candidate to study impurity-band conduction [\[4,5\].](#page--1-1) For most of III-V semiconductors such as GaAs [\[6,7\],](#page--1-2) InP [\[8\]](#page--1-3) and InSb [\[9,10\]](#page--1-4) doped with Mn concentration exceeding of a critical value, p-type conduction in a host crystal valence dominates the electrical transport at high temperature, while the nearest-neighbor hopping conductance (NNH) in impurity band appears at low temperature. For an extrinsic semiconductor with impurity conduction, the electrical conductivity is usually approximated by sum of the three components [\[11,12\]:](#page--1-5)

 $\sigma(T) = \sigma_{001} e^{-E_1/kT} + \sigma_{002} e^{-E_2/kT} + \sigma_{003} e^{-E_3/kT}$

where E_1 is related to the activation of conductivity in the host crystal valence band (or the conduction band), E_3 represents activation of NNH conductance, E_2 is related to the mechanism dominating in the intermediate temperature range of between the band and the hopping conductivity, and this kind of conductivity exists only at low compensation. Hopping conductivity is well known [\[11\]](#page--1-5) in samples with a high concentration of shallow centers. It occurs when the main contribution to the electrical conductivity comes from holes hopping directly between impurities without any excursion to the valence band with decreasing temperature and the gradual freezing-out of holes in the valence band. It is phonon-assisted, and the activation is related to the

dispersion of impurity levels due to random coulomb fields in a semiconductor. Hopping conductivity was subsequently studied in numerous investigations with germanium, silicon, gallium antimonide, diamond, and other semiconductors for long time.

The electronic properties of Mn in InAs samples grown by Czochralski were first measured with Mn concentrations up to 10^{19} cm³ [\[13\]](#page--1-6). It should be pointed out that, as in the case of other III-Vsemiconductors, manganese in InAs is an acceptor and InAs:Mn has p-type conduction at room temperature. From the ab initio density-function calculations for electronic structure of InMnAs [\[14\],](#page--1-7) it is found that Mn appears as an ionized acceptor, $Mn^{2+}(3d^5)$ or a neutral acceptor, $Mn^{2+}(3d^5)$ + hole. But the research on the detailed information of impurity band conduction of InAs:Mn is quite limit. Hence it is of great importance for us to study its electrical transport properties as a function of temperature.

In this paper, the electric transport properties of Mn-doped InAs wafers are interpreted in terms of valence bands and impurity band transport. Both samples are found to be p-type conductivity and Mn in InAs acts itself as a shallow acceptor. For lightly doped samples, the electrical transport properties are characterized by the valence band conduction. For heavily doped samples, temperature dependent Hall effect measurements was conducted, from which we can draw the conclusion for the nature of Mn impurity band at higher Mn concentration corresponding to the nearest hopping conduction confirming the existence of low temperature impurity band conduction which was analyzed detailed with the experimental results.

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2. Experimental

Mn-doped InAs wafers with different carrier concentration used in this work were sliced from different un-doped (100)-oriented Mn-doped InAs ingots grown in our laboratory by the liquid-encapsulated Czochralski (LEC) method. The high purity (99.99%) In, As and Mn metals were used as the starting materials. The impurity concentration was controlled by chemical and mass ratio methods. In order to obtain information about the number of acceptors or donors in InAs, Hall measurement was conducted to samples at temperature range of 77–300 K. It is found that Mn acts as shallow acceptor and it is regarded as complete ionization in InAs. The Hall coefficient was measured in a 0.5 T field, using the Van der Pauw method of reversals of current and magnetic field. The hole concentration was calculated from the Hall coefficient R_H using $p_0 = r_H/eR_H$, where the Hall scattering factor r_H was assumed to be unity for convenience and simplicity. The carrier concentration at room temperature of the two sample is determined to be 9.2×10^{17} cm⁻³ and 9.0×10^{18} cm⁻³, respectively. The sample with lower carrier concentration is named sample A, and the other one is sample B. To calculate the ionization energy of the Mn acceptor in InAs, low temperature Photoluminescence spectra (PL) was conducted on sample A.

3. Results and discussion

As is shown in [Fig. 1](#page-1-0), the resistivity of the two samples increases as a result of cooling at temperature range below 183 K, which is due to the freeze-out of holes. The Hall mobility of sample A decreases as increasing temperature, which is in the valence band transport regime. This behavior is in sharp contrast to heavily doped sample B, for which Hall mobility have obvious increase with the temperature increasing in the range of 77–223 K due to a dominance of ionized impurities scattering showing the characteristic of impurity band conductivity $[4,6]$. It is worth noting that the value of mobility for sample B is less than that of sample A obviously since the hole jumps are associated with a weak overlap of wave-function tails from neighboring acceptors for impurity band conduction [\[11\]](#page--1-5). But it wins in the competition with band conduction, because only a small number of shallow free carriers can participate in the latter.

The temperature dependence of the carrier concentration of sample A and B was measured as shown in [Fig. 2](#page--1-8). Hall effect measurements show that the conductivity of both the Mn-doped InAs samples was of ptype as in the case of InSb, GaAs and GaP. The hole concentration for sample A increases rapidly from 4.3 \times 10^{17} cm $^{-3}$ at 89 K to 9.2 \times 10^{17} cm−³ at 295 K showing normal semiconductor Hall results, and thermally activated transport related to ionization energy in the valence band dominates in this regime. Ionization energy of the Mn acceptor in most Ⅲ-Ⅴ semiconductors such as GaAs, InP and GaP have been studied in the previous literature [\[15\]](#page--1-9), but that is rarely reported about Mn acceptor in InAs. In order to obtain the ionization energy of the Mn acceptor in InAs single crystals, photoluminescence spectrum was measured at 10 K, as shown in [Fig. 2\(](#page--1-8)a) inset. There are three peaks located at 409 meV, 382 meV and 355 meV in PL spectra of sample A. The weak peak at about 409 meV corresponds to emission process between the conduction and valence band. From this peak, we extrapolate a value for the band gap at 10 K of 409 \pm 1 meV, which is less than the energy gap value of 415 meV of InAs single crystals [\[16\]](#page--1-10) at 10 K, since doping narrows the gap [\[14\].](#page--1-7) The main peak located at 382 meV is clearly due to conduction band-acceptor transition. And we attribute the peak at 355 meV to a phonon replica of the main peak. The shift between the band-to-band transition peak and the main peak is 27 meV, which is agreed with the activation energy reported in previous literature [\[7,17\]](#page--1-11). For comparison, effective mass theory predicts a shallow Mn acceptor in InAs to have an energy of 28.7 meV assuming a hole effective mass m_h^* of 0.33 and a relative dielectric constant ε of 12.5 [\[18\]](#page--1-12). From the small discrepancy, it is reasonable to confirm that the ionization energy of Mn acceptor in lightly doped InAs is 27 meV.

Different results of Hall effect appear for sample B as is shown in [Fig. 2](#page--1-8)(b). At temperature range of 77–183 K, an apparent increase of the Hall concentration while lowering the temperature can be visible indicating the presence of the NNH in impurity band [\[19\]](#page--1-13) related to jumping of holes between closest-lying acceptor sites (from occupied to empty acceptor sites). At temperatures above 183 K, the hole concentration does not change with temperature indicating both electrical transport in the valence band and the nearest hopping conductance in the impurity band are comparable in magnitude. The samples used in this experiment shows no ferromagnetism for Mn at compositions far less than 1 at%. The valence band deformation by doping is negligible and the Fermi level exists in impurity band [\[20\],](#page--1-14) which is not merged with valence band.

For sample B, the single degenerate impurity level is replaced by an impurity band of finite width in energy. At low temperature intrinsic carriers are frozen out, and a hole contributed by Mn acceptor localized near one of the Mn centers does not spread in time over other centers constituting this band. The characteristic distance at which an hole can be localized near a shallow impurity center (localization radius) a_0 is given by [\[21\]:](#page--1-8)

$$
a_0 = \sqrt{\hbar^2/2m^*E_1} \tag{1}
$$

where m^* is the hole effective mass of InAs and $E_1 = 27meV$. Basing on Eq. [\(1\)](#page-1-1) one obtains $a_0 = 1.7$ nm, which is larger than that of GaAs (1 nm), InP (0.9 nm) and GaP (0.3 nm), suggesting the appearance of weakly localized hole. In this case, Mn^{2+} centers traps a hole, thus forming a neutral acceptor $Mn^{2+}(3d^5)$ + hole which has some features of a weakly localized center. This weakly localized hole is responsible

Fig. 1. Resistivity and Hall mobility as a function of temperature of sample A (a) and sample B (b).

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