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The electrical properties and distribution of indium in germanium crystals

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ABSTRACT

Indium doped germanium crystals were grown in a hydrogen atmosphere using the Czochralski method. The electrical properties of indium doped germanium crystals were measured by Hall effect at 77 K. The axial and radial distributions of indium in the germanium crystals were investigated. The effective segregation coefficient of indium in germanium is determined to be 0.0009 with the concentration of indium from 3×10^{12}~1×10^{19} cm^{-3}. The interface shape between melt and crystal determined the radial distribution of indium in germanium crystals.

1. Introduction

Germanium crystals have a wide field of applications such as windows and lenses for IR optics, radiation detectors and substrates for high efficiency solar cells. The impurities will have effect on the electrical and optical properties of germanium. The group III elements (Boron, Aluminum, Gallium and Indium) are acceptor (p type) impurities in germanium crystal. Recently, the diffusion and implantation of indium in germanium have attracted intensive research interests [1–4]. As a p type dopant, the electrical properties and distribution of indium in germanium crystals had been studied in 1950s and 1960s [5,6]. At that time, the impurities in germanium raw ingot were higher than 10^{13} cm^{-3}. Even now, it is very difficult task to purify germanium ingot to impurity level lower than $< 10^{12}$ cm^{-3} that only few commercial companies (Umicore, Ortec, and Canberra) and a research group at the University of South Dakota [7–9] have achieved. Therefore, the electrical properties and distribution of indium in germanium crystal were investigated with doping level higher than 10^{13} cm^{-3} [10,11]. The original impurities in germanium ingot could bring in errors in the study of properties of target dopant in germanium crystal and make the analysis complicated when the doping level $< 10^{13}$ cm^{-3}.

Normally, the germanium crystals were grown in an inert atmosphere (like Helium and Argon) in graphite crucible by Czochralski method [12,13]. Graphite crucible contains boron and aluminum [14], which can be dissolved into germanium melt to increase the impurity concentration. High purity quartz crucibles have been verified to be the best container for germanium melt. Therefore, it is used for growing high purity germanium crystals [15]. However, the germanium can react with quartz crucible to bring the oxygen into germanium melt. Oxygen can form oxidation complexes acting as trap centers to affect the energy resolution of the germanium gamma ray detectors. Experiments showed when the doping level of boron and aluminum is lower than 10^{12} cm^{-3}, the effective segregation coefficient for boron disappears faster than the prediction by a theoretical model [14] and for aluminum approaches one, which is caused by boron and aluminum oxidation complexes [16–18]. When germanium crystal is grown in a hydrogen atmosphere, the concentration of oxygen in germanium crystal can be reduced. It will be interesting to study if the distribution of indium would be affected by the possible oxidation complexes.

Diameter of 3–12 cm high purity germanium crystals (impurity level $< 10^{11}$ cm^{-3}) have been grown in our group [7,8,19,20]. We can use highly pure germanium ingots to study the distribution and electrical properties of indium in germanium crystals. According to our knowledge, the distribution of indium in germanium crystal with doping level around 10^{12} cm^{-3} has not been investigated. Therefore, in this paper, we report the indium doped germanium crystal growth, the impact of indium concentration on the Hall mobility at 77 k, and the axial and radial distribution of indium in the germanium crystals.

2. Experiment

High-purity Germanium ingots (p-type with net carrier concentration $< 2 \times 10^{11}$ cm^{-3} at 77 K) of 3 kg in mass were charged in to a quartz crucible, which is 18 cm in diameter and 11 cm in depth. Indium (with a purity of 99.9999%) rods with doping concentration 2.94×10^{15} cm^{-3} and 9.73×10^{18} cm^{-3} were added to the crucible for each Ge crystal. Two < 100 > oriented germanium crystals with 8–9 cm in

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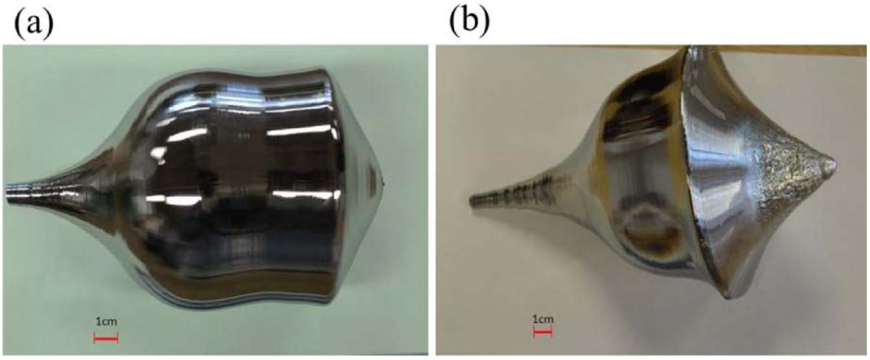

Fig. 1. (a) Crystal A with indium doping concentration 2.94 × 10^{15} cm^{-3} (b) Crystal B with indium doping concentration 9.73 × 10^{18} cm^{-3}.

diameter were grown by CZ (Czochralski) method at a pulling rate of 25 mm/h in a flowing gas atmosphere of high purity H_2 (5 N) with a flux of 150 l/h under a pressure of 1 atm. The rotation speed of the crystals was 3 rpm. In the finishing process, all the germanium melt must be pulled out completely; otherwise, the remaining melt will break the quartz crucible.

Fig. 1 shows the grown crystals. These crystals were cut into wafers at various positions along the grown axis by a diamond wire saw. Then, square specimens (1.5 × 1.5 × 0.15 cm^3) were cut from the wafers along the radial direction. These samples were polished, ultrasonically washed in a methanol, etched in HNO_3: HF (1:3) solution for 3 min, rinsed with deionized water, and dried with nitrogen gas. Ga-In (75.5:24.5 wt%) eutectic ohmic contacts were then scratched onto the four corners of the samples to be electrodes for Hall effect measurement. Finally, the samples were measured at 77 K (liquid N_2 temperature) using the Hall effect with the Van der Pauw geometry. An Ecopia HMS-3000 with a 0.55 T permanent magnet was used to make the measurements.

3. Hall effect of indium doped germanium crystals

According to the empirical expression for the intrinsic charge carrier density by Conwell [21], the numbers of free charge carriers are 2.5 × 10^{13} cm^{-3} at room temperature (300 K) and 1.9 × 10^{-6} cm^{-3} at liquid nitrogen temperature (77 K) for germanium. At 77 K, the group III and V elements are completely ionized impurities in germanium [22]. Hall effect measurement is an effective method to measure ionized impurities in germanium. Therefore, the Hall effect measurement can be used for measuring the indium concentration in germanium at 77 K without the interference from thermal generated free charge carriers.

The active-impurity concentration (N_A-N_D) is given by:

$$N_A - N_D = r/(\rho e\mu_{H(norp)}), \tag{1}$$

and

$$N_A - N_D = r/(eR_H), \tag{2}$$

where N_A is the concentration of acceptor (hole); N_D is the concentration of donor (electron); ρ is the resistivity; e is the electron charge, 1.6 × 10^{-19} C; μ_H is the Hall mobility associated with the carrier type of sample, n or p, according to whether R_H is negative or positive, respectively; r is Hall effect factor and depends on temperature, crystal type and crystal orientation; and R_H is the Hall coefficient.

The n type impurity is mainly phosphorus with concentration < 10^{11} cm^{-3} [7] and the p type impurities like gallium and aluminum are less than 2 × 10^{11} cm^{-3}. The total amount of other impurities is much less than the concentration of indium in grown crystals. The charge carriers are made predominantly of holes from the ionized indium atoms. Therefore, Eqs. (1) and (2) are modified to be:

$$N_A = r/(\rho e\mu_p), \tag{3}$$

and

$$N_A = r/(eR_H) \tag{4}$$

Hall coefficient R_H is measured in terms of the voltage produced across the Hall probes, per unit magnetic field (B) and current (I):

$$R_H = \frac{\Delta Vt}{IB} \tag{5}$$

where ΔV is the Hall voltage, t the thickness of the plate along the magnetic field.

According to Eqs. (3) and (4), the Hall mobility is determined by:

$$R_H = \rho\mu_H \tag{6}$$

The Hall mobility μ_H is related to the drift mobility μ by:

$$\mu_H = r\mu \tag{7}$$

where r is the Hall effect factor, which is 1.15 at 77 K for hole [23]. The poor contacts, effects of surface charge, macroscopic nonuniformity and inhomogeneities can make the measured Hall mobility lower than true values.

At 77 K, the drift mobility (μ) of hole in germanium is dominated by lattice-scattering mobility (μ_L) and ionized impurity scattering mobility (μ_I) [10,24]. The contribution of ionized impurity scattering mobility to the measured mobility can be estimated from Matthiessen's rule if the lattice-scattering mobility can be determined:

$$\frac{1}{\mu} = \frac{1}{\mu_L} + \frac{1}{\mu_I} \tag{8}$$

For holes, the lattice scattering mobility $\mu_L = 1.05 \times 10^9 T^{-2.33}$ [23], at 77 K, $\mu_L = 42234$ cm^2/vs which is close to the IEEE standard [25]. The ionized impurity scattering mobility can be calculated by Brooks-Herring equation [26,27]:

$$\mu_I = \frac{128\sqrt{2}\pi^{1/2}(\varepsilon_0\varepsilon_r)^2(k_BT)^{3/2}}{m^{*1/2}N_IZ^2e^3}\left(\ln\frac{24m^*\varepsilon_0\varepsilon_r(k_BT)^2}{N_Ie^2\hbar^2}\right)^{-1} \tag{9}$$

where N_I is the ionized impurity concentration, ε_0 is free space permittivity, ε_r is the relative permittivity of Ge, $m^* = 0.2\,m_0$ is the effective mass of hole [28], m_0 is the electron mass, $Z = 1$ is the effective charge number in Ge, k_B is the Boltzmann constant, and T is the temperature in Kevin.

The theoretical Hall mobility can be calculated by Eqs. (7)–(9) and is shown in Fig. 2. The measured Hall mobility has a good consistence with the calculated results. Thus the measured carrier concentrations of indium by Van der Pauw method are reliable.

4. The radial and axial distribution of indium doped in germanium crystals

Fig. 3 shows the radial distribution of indium concentration in different location of wafers. Center samples show lower indium concentration in comparing to the edge of samples. The indium concentration ratios of center and edge samples at different axial location (g) are shown in Table 1. The non-uniform radial distribution is caused