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LPE growth of InP layers from rare-earth treated melts for radiation detector structures

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ABSTRACT

Rare-earth (RE) elements present in the growth from the liquid phase have purifying effect on III–V semiconductors due to REs high affinity towards chemical species of shallow impurities. We demonstrate this purifying effect on the preparation of InP layers by liquid phase epitaxy with Pr admixture to the growth melt. We employ low temperature photoluminescence, capacitance–voltage and Hall effect measurements to show that optimized concentration of Pr admixture results in the growth of high purity layers of both conductivity types. We discuss the application of p-type InP layers in radiation detectors.

1. Introduction

First applications of rare-earth (RE) elements in semiconductor technology are rooted in radiation tolerance improvements of silicon solar cells and purification of GaP crystals. The idea was later adopted in the technology of germanium and compound semiconductors. Since the 1980s, considerable attention has been directed towards REs applications in III–V compounds both for epitaxial films and bulk crystals [1].

The uniqueness of REs arises from the fact that the lowest-energy electrons are not spatially the outermost electrons of the ion, and thus have a limited direct interaction with the ions environment. The shielding of the 4f electrons by the outer filled shells of 5p and 5s electrons prevents the 4f electrons from directly participating in bonding [2]. The RE ions maintain much of the character exhibited by a free ion. This non-bonding property of the 4f electrons is responsible for the well-known chemical similarity of different REs. Since transitions between the electronic states of the shielded 4f electrons give rise to spectrally narrow electronic transitions, materials containing REs exhibit unique optical properties. By careful selection of the appropriate ion, intense, narrow-band emission can be gained across much of the visible region and into the near-infrared [3]. Inspired by the striking results accomplished in the field of optical amplifiers and lasers based on RE-doped fibers [4], substantial research activity has been recently carried out on RE-doped semiconductor materials for optoelectronics [5].

In most cases, however, achieving effective doping of III–V compounds by REs during growth from the liquid phase has proven difficult; the high chemical reactivity and the low solid solubility are the main restrictions on introducing RE atoms into the crystal lattices [6]. On the other hand, the enhanced chemical affinity of REs towards most species of the shallow impurities leads to the formation of insoluble aggregates in the melt. Under suitable growth conditions, these aggregates are rejected by the growth front and are not incorporated into the grown layer: gettering of impurities takes place. Removal of detrimental impurities is of vital importance in applications such as PIN photodiodes [7] or nuclear particle detector structures [8] where high electron and hole drift velocities are appreciated.

InP single crystals, both bulk crystals and thick epitaxial layers, are promising materials for the preparation of radiation detectors operating at room temperature (RT). The RT operation with low-noise performance is expected due to its large bandgap energy E_g = 1.35 eV. The high value of atomic number of In and high mass density of InP ensure a high stopping power [9]. High purity and homogeneity of the layers is essential to attain a large charge collection efficiency. Conventionally prepared bulk and epitaxial InP crystals are of n-type conductivity due to intrinsic donor impurities. The lack of a rectifying contact on n-type InP results in high leakage currents which must be reduced by cooling. Schottky contacts with a large barrier height can be prepared solely on p-type InP [10]. p-Type InP is commonly prepared by intentional doping with shallow acceptors. However, the purity of these layers is not sufficient for their consideration in radiation detectors. We show that

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intentional doping can be avoided by the preparation of p-type InP from Pr treated melts by liquid phase epitaxy.

2. Experimental

A conventional sliding boat system was available for the growth of InP layers by LPE. InP epitaxial layers were prepared by the supercooling technique on (1 0 0)-oriented substrates with Pr addition to the melt. The role of growth conditions, particularly (i) the growth temperature, (ii) the cooling rate, (iii) the growth time, and (iv) the method of the growth melt preparation were investigated together with varying Pr content in the melt. The initial growth temperature was altered from 615 to 660 °C with the initial supercooling of 5–10 °C and the cooling rate of 0.3–0.7 °C/min. The growth was terminated after 20–30 min. The layer thickness varied from 7 to 15 μm. To suppress the great affinity of Pr, especially with respect to oxygen and hydrogen, it was necessary to prevent the reactive metallic Pr to come into contact with the surrounding ambient at the stage before the growth process. The LPE process was realized in two cycles. In the first cycle, required amounts of In and undoped polycrystalline InP were homogenized at the temperature of 700 °C for 1 h in the Pd-purified hydrogen ambient. The system was cooled, and in the second cycle, pieces of Pr were mechanically embedded into the melt to form the growth solution. A polished single crystal (1 0 0)-oriented semi-insulating InP:Fe or n-type InP:Sn substrate was placed in the moving part of the boat. The substrate was covered by an InP slide to suppress its thermal decomposition. The temperature was again raised to 700 °C and held constant for 1 h. The system was then cooled down to the growth temperature. Just prior to growth, the substrate was etched in situ by pulling the melt solution of pure In on substrate.

Structural defects were revealed by using several chemical etchants. Optical microscopy with Nomarski differential interference contrast was employed to study the surface morphology and the structural defect density. Scanning electron microscopy (SEM) served to trace the substrate–layer interface and the layer thickness after chemical etching. Estimates of the electrical properties on the contactless samples were gained from capacitance–voltage (C–V) measurements performed with the mercury probe at room temperature. In the probe, two concentric circular Schottky contact with the diameter of 3 and 0.3 mm are formed under the pressure of 20 Torr. Capacitance is monitored by a bridge with the test frequency of 1 MHz. The samples prepared on SI substrates were further characterized by the temperature dependent Hall effect measurement using a home made computer controlled apparatus with high impedance inputs and a switch box in van der Pauw configuration. The current source and current sink can be individually applied to any sample contact. The error voltages are eliminated by taking eight dc measurements of the Hall voltage at each temperature with two directions of the magnetic field. The set-up is equipped with a closed-cycle helium cryogenic system for the temperature range 6–320 K or with a liquid nitrogen cryostat for the temperature range 80–450 K. Photoluminescence (PL) spectra were taken at various temperatures and various levels of excitation power. The low temperature measurements were performed in order to gain information on the impurity and defect states, since the thermal energy is low enough and a variety of transitions can be resolved. The experimental set-up consists of an optical cryostat, a monochromator and a detection part. The optical cryostat is based on a closed cycle helium refrigeration system and automatic temperature controller that makes possible measurements in the interval of 4–300 K. PL spectra are analyzed by 1 m focal length monochromator coupled with nitrogen-cooled Ge detector or S1 photomultiplier. The excitation was provided by the He–Ne and Ar ion laser. The excitation densities varied in the range of 0.1–600 mW/cm^2 using suitable neutral density filters.

3. Results and discussion

We demonstrate the gettering phenomenon on InP epitaxial layers prepared from praseodymium treated melts. Dependence of the impurity concentration on the Pr content in the growth solution determined by C–V measurements is depicted in Fig. 1. By increasing Pr content in the growth solution, simultaneous gettering of shallow impurities occurs. Donor impurities are preferentially gettered due to REs high affinity towards Si and group VI elements [11]. This preferential gettering leads to the conductivity conversion from n- to p-type. Further increase of Pr addition results in moderately elevated acceptor concentrations. We claim that there are two mechanisms behind this elevation. First, new acceptor species are introduced into the growth solution with Pr. The 3N purity of Pr, which is currently the highest purity available on the market, is much lower than that of 6N In and InP source materials. At low concentrations of Pr, the gettering effect remains virtually undisturbed. However, when Pr concentration exceeds the amount necessary for the removal of all donor species, the inadvertent introduction of impurities with Pr admixture to the growth solution takes place and results in elevated acceptor concentrations in the grown layers. Second, RE pnictides – particularly compounds of P and Pr – are formed in the growth solution. Consequently, the stoichiometric ratio of In and P is altered at the growth interface so that the generation of P vacancies is favored [12]. The increased number of vacancies results in increased p-type activity of amphoteric impurities.

The PL spectra show fine features with narrow peaks supporting the results of C–V measurements. Typical PL spectra comparing layers grown with and without Pr admixture are shown in Fig. 2. The band at highest energy (BE) exhibits superlinear behavior with increasing excitation power and results from the decay of excitons. Transitions due to free exciton (FE) and excitons bound to the neutral donor (D^0, X) or the neutral acceptor (A^0, X) are well resolved. Transitions described as B–A and D–A are related with shallow acceptors and correspond to conduction band–acceptor and donor–acceptor pair transitions, respectively as revealed by the examination of their temperature dependence (see Fig. 3). The band of the lowest energy is rapidly quenched around 25–30 K and is thus assigned to D–A transitions. The other sub-band quenches around 70 K and is thus assigned to B–A transitions [13]. The peak LO is a phonon replica of the peak related to shallow impurities and its position is in accordance with the known value of 43 meV for

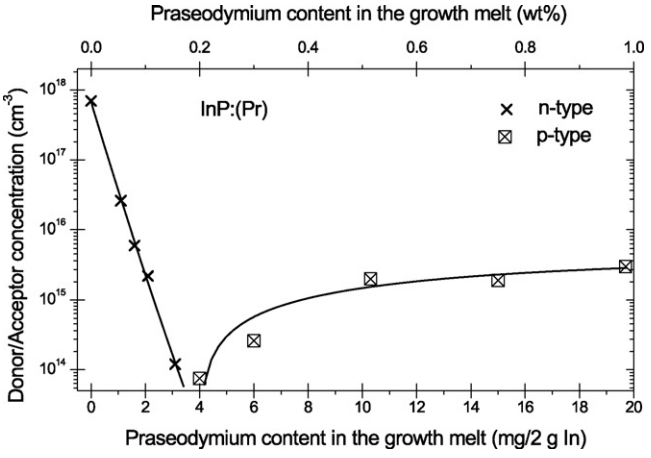

Fig. 1. Dependence of the donor/acceptor concentration on Pr content in the growth solution. The growth temperature was 630 °C, the cooling rate 0.7 °C/min, and growth duration 30 min.