蒸気圧制御InxGa1-xPに関する研究

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論文内容要旨

The semiconductors having direct optical transition energy gap $E_g \geqq 1.8$ eV are attrative for light emitting diodes (LED) because the eye is only appreciable sensitive to light of energy in this range and no need of momentum conservation for direct band gap materials. Techniques of economically growing the semiconductors must be made available for batch fabrication of LED's. High probability of radiative recombination with a high quantum efficiency is, of course, one of the basic requirements of the semiconductor materials.

Recently, $In_xGa_{1-x}P$ is industrially interesting semiconductor material for the fabrication of LED's and laser diodes because its energy gap can vary with composition and having the direct energy gap of 2.1−2.2 eV (300°K) at $0.6 \leqq 1-x \leqq 0.7$. Significant growth technology is still needed for $In_xGa_{1-x}P$ material.

The new epitaxial growth method called temperature difference method under controlled−vapor−pressure (TDM−CVP) is presented.

Chapter 2 described the epitaxial growth and crystal growth of $In_xGa_{1-x}P$ by means of TDM−CVP. The suitable temperature programme for epitaxial growth was found by experimentally. The interface linearity between the epi−

taxial layer and substrate was found to depend on the temperature programme. The experiments of epitaxial growth were performed under such varying valuables of parameter as the growth time, the growth temperature and phosphorus pressure. Results of $In_xGa_{1-x}P/GaP$ experiments lead to the conclusions as follows : (1) The composition does not change with the applied phosphorus pressure. Therefore, the lost of phosphorus from the solution can neglect for TDM−CVP. (2) The thickness of epitaxial saturates at a certain growth time. The reaction of phosphorus and indium can neglect. (3) The composition of epitaxial layer remains constant for whole thickness grown under the same growth temperature. It shows that source comes down with constant rate to the lower temperature region.

The $In_xGa_{1-x}P$ bulk crystals were grown by TDM−CVP under different conditions. The temperature programme for bulk crystal growth was described. By using the growth steps procedure, large single crystals were obtained. The relation between the phosphorus pressure and half−width of X−ray diffraction trace for $In_xGa_{1-x}P$ bulk crystal grown by TDM−CVP is shown in Fig. 1. It shows that phosphorus pressure controls the half−width of X−ray spectra. At a certain phosphorus pressure, the half−width has a minimum value. But the temperature difference could not control the half−width.

The epitaxial growth of $In_xGa_{1-x}P$ on $In_xGa_{1-x}P$ substrate was also done by TDM−CVP. No research paper concerns with the epitaxial growth of $In_xGa_{1-x}P$ on $In_xGa_{1-x}P$ can find because $In_xGa_{1-x}P$ substrate is difficult to obtain.

Chapter 3 described the fabrication of p−n junction by TDM−CVP. I−V characteristic of the diode was also investigated. Cleaved surface of $In_xGa_{1-x}P$ p−n junction was also described. Result of electron probe microanalysis of junction was shown.

Chapter 4 described the experimental results of electrical properties, optical properties and surface morphologies of $In_xGa_{1-x}P$ epitaxial layer and bulk crystal.

Relation between the phosphorus pressure and the impurity concentrations was investigated. It was known that phosphorus pressure controlled the impurity concentrations. At a certain phosphorus pressure (optimum pressure), the impurity concentrations was minimum. Relation between the phosphorus pressure and mobility is shown in Fig. 2. Mobility also depends on the phosphorus pressure $In_{0.2}Ga_{0.8}P$ crystal grown by TDM−CVP has the mobility of 1582㎠/v sec.

This value is larger than any published value for $In_xGa_{1-x}P$ crystal.

Relation between the impurity concentrations and composition of $In_xGa_{1-x}P$ was also described in this chapter.

Photoluminescence (P. L) intensity and half-width of $In_xGa_{1-x}P$ also depended on the phosphorus pressure (P_{InGaP}). This relation is shown in Fig. 3. The intensity is maximum at a certain phosphorus pressure. At lower phosphorus pressure, the photoluminescence intensity is low and increases with phosphorus pressure to the optimum pressure and decreases at higher pressure. The half-width is minimum at the optimum pressure. The peaks of photoluminescence spectrum were also found to depend on the phosphorus pressure. Some peaks were suppressed by applying appropriate phosphorus pressure.

The surface morphologies of both $In_xGa_{1-x}P$ epitaxial layer and bulk crystal grown by TDM-CVP were also described in this chapter. The cleaved surface morphologies were studied with respect to the phosphorus pressure. The cleaved surface of $In_{0.18}Ga_{0.82}P/GaP$ grown under phosphorus pressure of 46 Torr. was better than that grown under phosphorus pressure of 9.44 Torr. and 197 Torr. The morphologies of surfaces and cleaved surfaces of epitaxial layers of difference composition were also described.

The epitaxial layer surfaces morphologies also depended on the phosphorus pressure. Microsteps and some inclusions were observed in the epitaxial layer of $In_{0.33}Ga_{0.67}P$ grown under phosphorus pressure of 94 Torr. and 122 Torr. at the growth temperature of 745℃. The surface of epitaxial layer grown under 45.8 Torr. was not so smooth but freed of inclusions. The surface morphology depends on the type and density of nucleations. Therefore, phosphorus pressure may control the formation of initial nucleations.

The surfaces morphologies of $In_xGa_{1-x}P$ bulk crystals grown by TDM-CVP were also found to depend on the phosphorus pressure. The X-ray diffraction pattern of bulk crystals were also shown in this chapter. Single crystal of $In_xGa_{1-x}P$ was successfully grown by TDM-CVP.

Chapter 5 described the relation between the optimum phosphorus pressure and the growth temperature. The optimum phosphorus pressure depended on the growth temperature.

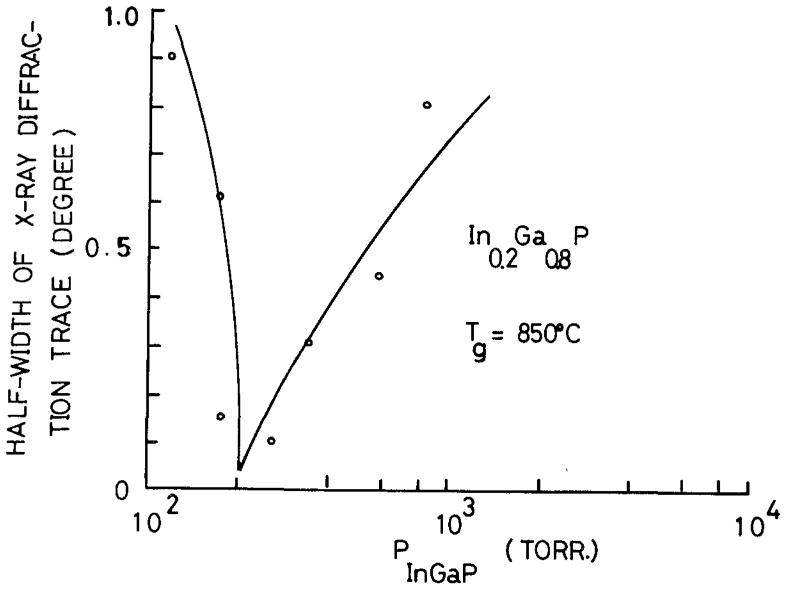
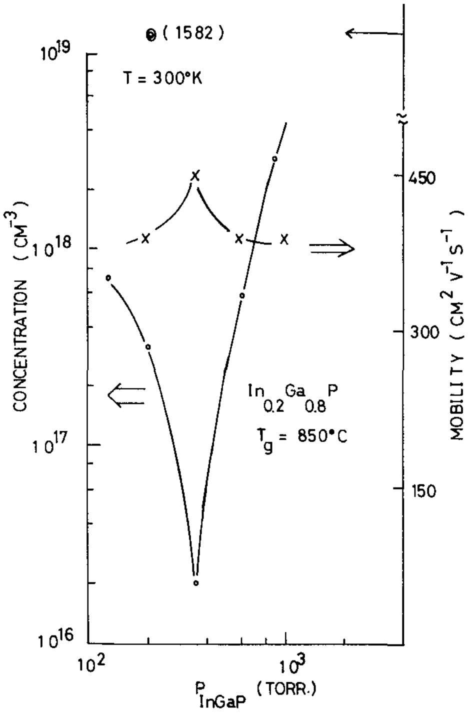


Fig. 1 Relation between the phosphorus pressure and half-width of X-ray diffraction trace for $In_xGa_{1-x}P$ bulk crystal

Fig. 2 Relation between the carrier concentration and mobility of bulk crystal with the phosphorus pressure



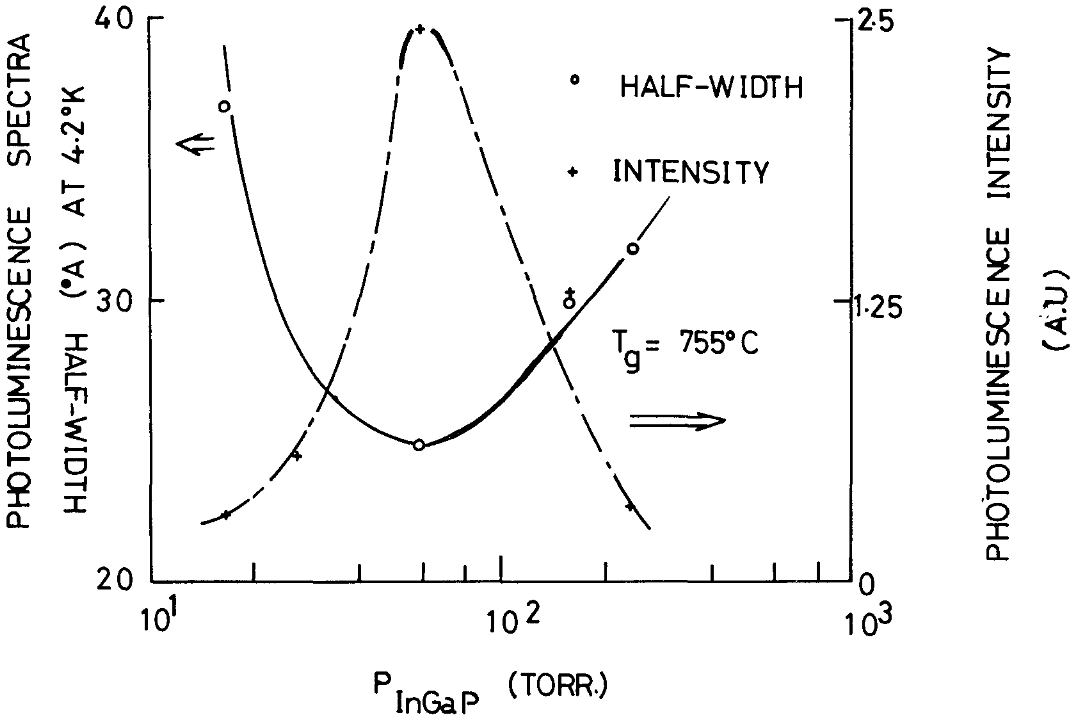


Fig. 3 The P.L spectra intensity and half-width of $In_xGa_{1-x}P$ epilayer grown on $In_xGa_{1-x}P$ substrate as a function of P_{InGaP}

審査結果の要旨

(In−Ga)P結晶は移動度が大きいことや，直接遷移型半導体で黄から緑に亘る発光材料として有望なことなどで近年注目を集めている材料である。しかるに燐の蒸気圧が高いために結晶成長中や加工中に燐が蒸発して化学量論的組成よりずれることが多い。

本論文は，結晶成長中にも燐の蒸気圧を印加しながら，(In−Ga)P結晶を育成し，完全性の高い結晶を得ることを目的として研究した結果についてまとめたもので，序論・結論及び本文3章よりなる。

第1章は序論であって，本研究の企画された背景及び本研究の目的について述べたものである。第2章より本論に入り，本研究に用いた蒸気圧を一定に保ちながら温度差を結晶析出部と素材結晶との間に与えて均一な結晶を得る方法及び装置について説明している。次いで温度を若干振動させることにより，ブリッジマン法によって1㎜程度の可成大きな結晶を得，X線回折曲線の半値幅0.1°の可成良質な結晶であることを確かめている。このとき，InとGaの組成比は1%以下の変化で殆んど完全に均一な結晶であるとしている。また，加えた蒸気圧はGaとInの組成比には殆んど影響を与えないがX線回折曲線の半値幅は10倍近い変化を与えることを100Torrから1000Torrの間で測定し，850℃で結晶成長させるとき200Torrが最も妥当な蒸気圧であるとしている。

更にGaPを基板として及びブリッジマン法で得た結果を基板として，液相成長によって育成した成長層について同様の実験を行い，同様の結論を得ている。これらは，新しい重要な知見である。

第3章では，同様の技術を用いてGaP基板上に(In−Ga)P結晶を2度育成してpn接合を形成し，可成良好な電流電圧特性を得て，前章までに得た結果の裏付けを行ってい。

第4章は，得られた結晶の電気的特性及び光効果に関する測定結果と表面や断面の顕微鏡観察の結果をまとめたものである。結晶の品位を現わす1つの量と考えられる移動度は常温で1600㎠/V・sec程度であるが従来発表された結果のうち最高の値である。また，結晶中のキャリア密度の測定を行い，成長した組成と禁制帯幅の関係からほぼ説明できるとしている。

フォトルミネッセンスの測定からは多くの深い準位の密度が，結晶成長時に加えた蒸気圧によって変化することを示し，多くの実測結果を得ている。第5章は結論である。

以上要するに，本論文は従来全く得られていなかったと言える均一な(In−Ga)P結晶を成長させる方法を確立すると共に，その特性を明らかにしたもので，電子材料工学に資するところが少なくない。

よって，本論文は工学博士の学位論文として合格と認める。