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Comparative Study of Photoluminescence in Ordered and Disordered $Ga_{0.5}In_{0.5}P$ Alloys under Hydrostatic Pressure

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We have measured the photoluminescence (PL) spectra of ordered GaInP alloys grown by organometallic vapor phase epitaxy (OMVPE) at three different growth temperatures (Tg = 600, 650, and 700 ℃) as a function of pressure up to about 4.0 GPa at a temperature of 300 K. We have also done similar measurements on a disordered (bulk) alloy for comparison. We find that the band-gap energy E_o, derived from the PL peak spectra, of ordered alloys shows a sublinear pressure dependence and is significantly different from that of the disordered sample. The overall shift of E_o with pressure up to 3.5 GPa for the ordered sample grown at 700 ℃ is smaller than for both the ordered material grown at 600 ℃ and the disordered sample studied. The observed behavior of E_o can be related to the existence of a CuPt-type ordered structure in which the degree of ordering depends on Tg and the repulsion between Γ-folded states affects the band-gap energy.

1. INTRODUCTION

$Ga_{0.5}In_{0.5}P$, lattice matched to GaAs substrates, have been remarkable Ⅲ-Ⅴ materials that have the highest direct band-gaps among the commonly used Ⅲ-Ⅴ compounds. However, for the case of $Ga_{0.5}In_{0.5}P$ grown by OMVPE, it is found that the band-gap energy is anomalously smaller by about 50-100 meV when compared with other growth methods, such as liquid phase epitaxy (LPE). This has lead to $Ga_{0.5}In_{0.5}P$ grown by OMVPE being investigated by photoluminescence (PL),[1,2] transmission electron microscopy (TEM),[2,3] Raman scattering,[3,4] and electroreflectance (ER).[3,5] From TEM studies it was recognized that the anomalous band-gap energy depends on the degree of ordering, however, the relationship between the anomalous value and the degree of ordering is quite complex.

Pressure is often used as a tool to examine the band structures of semiconductors. In most Ⅲ-Ⅴ semiconductors, increasing pressure primarily causes an increase in the Γ- and L-conduction bands while inducing a small lowering in the X band. These effects are large enough to be observed by optical and electrical measurements. We have previously reported and discussed pressure dependence of PL spectra in OMVPE $Ga_{0.5}In_{0.5}P$ at 77K.[6] The relationship between the direct band-gap and ordering at atmospheric pressure does not give a full understanding.

In this work we have compared PL spectra for a series of OMVPE $Ga_{0.5}In_{0.5}P$ (ordered) alloys grown at different growth temperatures and bulk (disordered) alloy, as a function of pressure at a temperature of 300 K. These experimental results are also discussed in connection with the recent theoretical predictions[7,8] to the physical mechanism for the characteristic changes in the energies of the electronic states in the CuPt-type crystalline structure absent in disordered alloy.

2. EXPERIMENTAL

The OMVPE $Ga_{0.5}In_{0.5}P$ alloys were grown at one atmosphere from tricthylgallium, trimethylindium, and phosphine at a Ⅴ/Ⅲ ratio of 160. Growth temperatures (Tg) of 600, 650, and 700 ℃ were used.[2] Undoped $Ga_{0.5}In_{0.5}P$ epitaxial layers with a thickness of 0.7 μm were grown on Si-doped GaAs wafers with (001) orientation after the growth of a 0.4 μm GaAs buffer layer. The lattice mismatch was less than 10^{-3} for all samples. The existence of the ordered structure in these samples was confirmed by transmission electron diffraction (TED) observation.[2] Bulk alloy was grown by Bridgman method. PL measurements at 300 K were made with a diamond-anvil high-pressure cell.[9] We used methanol : ethanol = 4 : 1 as a pressure-transmitting medium. PL measurement was performed under excitation by a focused 514.5 nm Ar^+ ion laser.

3. RESULTS AND DISCUSSION

It is found that at atmospheric pressure PL peak energy (E_o) for the ordered samples is smaller than that for the bulk alloy, which has a minimum value at around Tg = 650 ℃, as previously reported.[1] Typical PL spectra of $Ga_{0.5}In_{0.5}P$ alloys gradually shift to higher energies with increasing pressure, and quench at around P = 4 GPa (Fig. 1). PL spectra of bulk alloy at 300 K quench at P = 3.5 GPa due to the pressure-induced Γ-X crossover. The PL half-widths for both ordered alloys and disordered alloy are nearly constant.

Figure 2 shows the pressure dependence of the PL peak energy for samples grown at 600, 650, 700 ℃, and bulk alloy, respectively. Although at 77K the

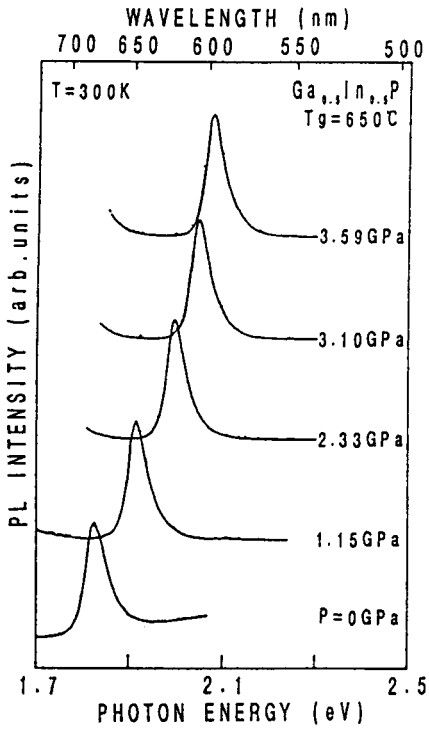

Fig. 1. Typical PL spectra of $Ga_{0.5}In_{0.5}P$ at several pressures. The growth temperature is 650 ℃.

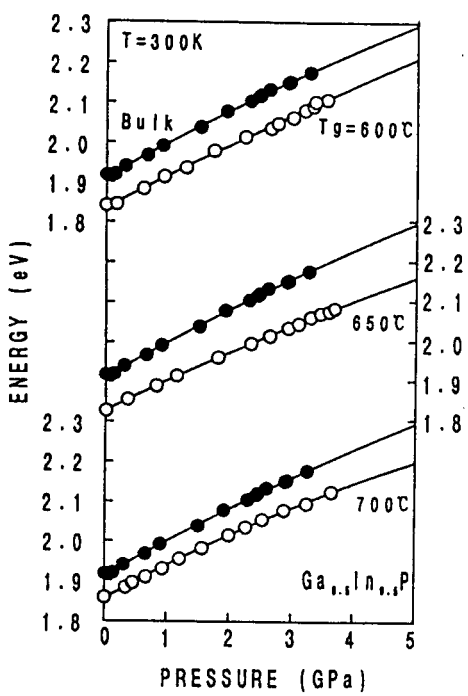

Fig. 2. Pressure dependence of the PL peak energy in ordered $Ga_{0.5}In_{0.5}P$. The growth temperatures are 600, 650, and 700 ℃, respectively (open circles). Closed circles are the data for PL peak energy in disordered alloy. The solid lines represent the least-squares fits to the experimental data.

shift of PL spectra saturates at a certain pressure 3.8-4.0 GPa, and then the PL spectrum tends to shift to lower energies,[6] similar behavior cannot be obtained at 300 K. In Fig. 2 the variation of PL peak energy with pressure in disordered alloy is located at a higher energy than those in the ordered alloys studied here. The difference between PL peak energies of ordered alloys and disordered alloy gradually increases with pressure, respectively. Such effect is also enhanced with increasing Tg.

A least-squares fit to the data shows a quadratic dependence. The pressure coefficients are given in Table I. The linear coefficients b of ordered alloys are smaller than that of disordered alloy. The quadratic coefficient c of ordered alloys increases with Tg. This indicates that the higher Tg sample (Tg = 700 ℃) shows a more sublinear pressure dependence than the lower Tg samples (Tg = 600, 650 ℃). It is found that total shifts up to 3.5 GPa, $E_0(3.5) - E_0(0)$, of ordered alloys is smaller than that of disordered alloy. These results strongly depend on Tg, consequently these results are closely related to the degree of ordering.

This sublinear behavior can partly be explained by the nonlinearity in the relationship between pressure and lattice constant.[10] However, this cannot describe the pressure dependence, which is different from each sample depending on growth conditions. We attempt to explain the pressure dependence of E_0 in ordered alloys using the model of repulsion obtained by Zunger et al (Fig. 3).[8] $Ga_{0.5}In_{0.5}P$ alloys grown by OMVPE order into CuPt-like structure, which is a superlattice along <111> direction. Hence, L states can fold into Γ states in the CuPt-type ordered structure. The interaction between Γ and Γ-folded L states repels each other by an amount that is inversely proportional to their unperturbed energy difference $\Gamma_{1c} - L_{1c}$ in the conduction bands and directly proportional to the square of the coupling matrix $(\triangle V)^2$. This repulsion lowers $\bar{\Gamma}_{1c}$ and rises $\bar{\Gamma}(L_{1c})$, thus reducing E_0. The denominator $\Gamma_{1c} - L_{1c}$ of this expression decreases with pressure, and the value of

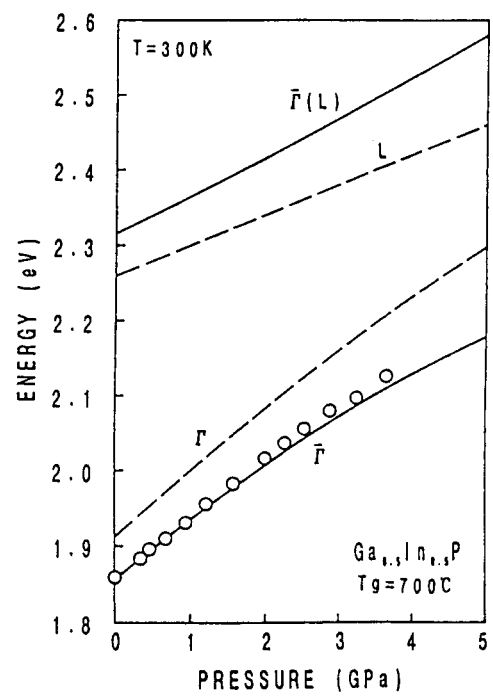

Fig. 3. Calculated band energies for $Ga_{0.5}In_{0.5}P$ grown at 700 ℃ as a function of pressure, considering the repulsion between Γ-folded states. Open circles are experiental data.

Table I. Data related to the band-gap of GaInP at high pressure: direct band-gap E_o at atmospheric pressure, its linear and quadratic pressure coefficients b and c, total shift up to 3.5 GPa, $E_o(3.5)-E_o(0)$, and difference between calculation and experimental results at 3.5 GPa $\bar{\Gamma}_{1c}(3.5)-E_o(3.5)$.

sample	E_o (eV)	b (meV/GPa)	c (meV/GPa^2)	$E_o(3.5)-E_o(0)$ (meV)	$\bar{\Gamma}_{1c}(3.5)-E_o(3.5)$ (meV)
Tg = 600 ℃	1.83	81.1	-1.23	269	37.3
650 ℃	1.82	78.0	-2.24	245	28.3
700 ℃	1.85	86.6	-3.53	260	15.5
bulk	1.91	90.4	-2.66	284	----

repulsion increases, thus influencing the quadratic coefficients c. In the calculations, the numerator $(\triangle V)^2$ was assumed to be pressure-independent, or nearly constant. As for the pressure coefficients of Γ_{1c}, the values of disordered alloy obtained here were used (Table I). L_{1c} was taken to be 2.26 eV at atmospheric pressure,[11,12] and increase linearly at a rate of 40 meV/GPa in common with other Ⅲ-Ⅴ semiconductors.

It is found that the calculated results tend to approach to our experimental results with increasing Tg. The diffences between calclations and experimental results at 3.5 GPa, $\bar{\Gamma}_{1c}(3.5)-E_o(3.5)$, reduce with Tg as shown in Table I. In other words, our experimental results for the highest Tg sample are theoretically better explained. It reflects the fact that a short-range ordered structure forms at lower Tg and gradually changes into highly long-range ordered structure with an increase in Tg within 600-700 ℃. Thus it seems that the differences in pressure dependence are closely related to ordering-induced changes in optical transitions as predicted by Zunger et al.[8,9]

4. CONCLUSIONS

We have measured the PL spectra of ordered $Ga_{0.5}In_{0.5}P$ alloys grown by OMVPE and disordered $Ga_{0.5}In_{0.5}P$ alloy and made a comparison between the ordered alloys and disordered alloy. It was clear that the pressure dependence of ordered alloys and disordered alloy are significantly different. We calculated $\bar{\Gamma}_{1c}$ using the model of repulsion and estimated our experimental results. It was found that the pressure dependence of E_o in OMVPE $Ga_{0.5}In_{0.5}P$ is closely related to the degree of ordering.

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REFERENCES

1) A. Gomyo, K. Kobayashi, S. Kawata, I. Hino, T. Suzuki, and T. Yuasa, J. Cryst. Growth 77 (1986) 367.
2) M. Kondow, H. Kakibayashi, and S. Minagawa, J. Cryst. Growth 88 (1988) 291.
3) M. Kondow, H. Kakibayashi, S. Minagawa, Y. Inoue, T. Nishino, and Y. Hamakawa, Appl. Phys. Lett. 53 (1988) 2053.
4) M. Kondow, and S. Minagawa, J. Appl. Phys. 64 (1988) 793.
5) T. Nishino, Y. Inoue, Y. Hamakawa, M. Kondow, and S. Minagawa, Appl. Phys. Lett. 53 (1988) 583.
6) T. Kobayashi, and R. S. Deol, Appl. Phys. Lett. 58 (1991) 1289.
7) J. E. Bernard, S. -H. Wei, D. M. Wood, and A. Zunger, Appl. Phys. Lett. 52 (1988) 311.
8) S. -H. Wei, and A. Zunger, Appl. Phys. Lett. 56 (1990) 662.
9) T. Kobayashi, Rev. Sci. Instrum. 56 (1985) 255.
10) B. Welber, M. Cardona, C. K. Kim, and S. Rodriguez, Phys. Rev. B12 (1975) 5729.
11) A. -B. Chen, and A. Sher, Phys. Rev. B23 (1981) 5360.
12) D. Auvergne, P. Merle, and H. Mathieu, Solid State Commun. 21 (1977) 437.