The Effect of Selenium Doping on the Optical and Structural Properties of Ga$_{0.5}$In$_{0.5}$P

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Selenium doping at an electron concentration of $10^{18} - 10^{19}$ cm$^{-3}$ is shown to cause an increase in both the band gap and the disorder of Ga$_{0.5}$In$_{0.5}$P films grown by metal-organic chemical vapor deposition on GaAs substrates. The effect of selenium is shown to be very similar to that of the $p$-type dopants, zinc and magnesium. Selenium doping is also shown to have a dramatic smoothing effect on the surface morphology of Ga$_{0.5}$In$_{0.5}$P films.

Key words: GaInP, MOCVD, order, disorder, band gap, dopant effects, morphology

INTRODUCTION

Ga$_{0.5}$In$_{0.5}$P (hereafter GaInP$_2$) has recently attracted considerable attention for both technological and scientific reasons. Because it is lattice matched to GaAs and has a band gap in the visible, it is an excellent material for diode lasers, light-emitting diodes, and cascade solar cells. Scientifically, it is of interest because its band gap, at constant composition, varies with growth parameters. This anomalous variation has been related to spontaneous ordering of the Ga and In on the group III sublattice. This spontaneous ordering apparently occurs by a surface mechanism in spite of the fact that the bulk disordered structure has been shown, both theoretically, and experimentally, to be lower in energy.

Recently, zinc and magnesium doping have been shown to decrease the ordering and increase the band gap of GaInP$_2$ films when the $p$-type carrier concentration exceeded about $10^{18}$ cm$^{-3}$. Because zinc has often been used as a catalyst for disordering of various superlattices, it was hypothesized that the mechanism for the $z$- and magnesium-induced disordering was related to diffusion of the $p$-type dopants through the growing film. The current study reports selenium-induced disordering similar to that reported for zinc and magnesium. This is unexpected since selenium usually diffuses much more slowly than zinc and magnesium, and since selenium is an $n$-type dopant, residing on the group V, instead of the group III sublattice. We also report a smoothing effect of selenium doping on the surface morphology of GaInP$_2$.

EXPERIMENTAL METHOD

The GaInP$_2$ films were grown by atmospheric pressure chemical vapor deposition using trimethylgallium, trimethylindium, and phosphine. Hydrogen selenide was used as the dopant source, giving very similar results to those reported previously. The vertical-flow quartz reactor utilizes a SiC-coated, inductively-heated graphite susceptor. Hydrogen, diffused through palladium, was used as the carrier gas. GaAs wafers, 2° off (100) toward (110), were used as the substrates after cleaning with 2:1:10 aqueous NH$_3$, H$_2$O$_2$, and H$_2$O. The films were grown in 20 min, 2 µm thick.

The carrier concentrations were measured by an electrochemical capacitance-voltage technique, using a Polaron profiler. Van der Pauw-Hall effect measurements were done on some of the samples. The absolute accuracy of the carrier concentration measurement was a factor of two, while the precision was 10-20%. The two methods agreed well. The selenium content of the films is not necessarily equal to the electron concentration. At very high selenium contents the electron concentration falls dramatically. The films with high selenium content, but low electron concentration, had band gaps and ordering more consistent with lightly-doped films. We report here only the carrier concentration, since the absolute selenium content has a less consistent effect on the band gap and ordering.

The lattice mismatch was measured by double-crystal, rocking-mode x-ray diffraction. All samples reported here exhibited a relative lattice mismatch of less than 0.001. Corrections to the band-gap energy for any deviations from the lattice-matched composition were less than 5 meV.

The band gaps were measured by electrochemical photocurrent spectroscopy. Figure 1 shows examples of the data. The photocurrent generated by light from a monochromator is plotted as a function of photon energy, $E$. The band gap, $E_g$, was obtained by fitting the photocurrent to Eqs. 1 and 2.

$$\text{photocurrent} = \text{constant} / (1 + 1/\alpha L) \quad (1)$$

where $L$ is the minority carrier diffusion length and $\alpha$ is the absorption coefficient. $\alpha(E) = \text{constant}*(E - E_g)^{1/2} \quad (2)$

A correction to $E_g$ was made for the Burstein-Moss effect for those samples with carrier concentrations higher than $3 \times 10^{18}$ cm$^{-3}$. This correction is nec-
RESULTS AND DISCUSSION

Table 1 summarizes the data, including the band gaps, corrected band gaps, carrier concentrations, and amount of order for each of the films at the three growth temperatures, \( T_g \), studied. The ordered volumes, reported as "medium, weak, very weak and disordered," we believe to correspond to 10–50%, \(-1\%\), <0.1%, and not detectable, respectively. At each growth temperature an increase in the selenium content leads to an increase in the band gap and a decrease in the observed amount of ordering. For films grown at 670°C an abrupt decrease in the ordering occurs at a carrier concentration of \( 10^{19} \) cm\(^{-3} \). At the same carrier concentration, an increase in the band gap is also observed. The uncertainty in the band gap of the highly doped film is large both because of uncertainty in the model of the Burstein-Moss effect and because the high carrier concentration (small minority carrier diffusion length) causes a shallow edge on the photocurrent, as seen in Fig. 1, decreasing the precision and accuracy with which the band gap can be measured. The photoluminescent (PL) line width also increased so that measurement of the band gap by PL presented no advantage over the method used. It is not possible to determine whether the small increase in the "apparent" band gap for the films doped to \( 5 \) and \( 7 \times 10^{18} \) cm\(^{-3} \) is caused by the Burstein-Moss effect or whether it is a result of less-extensive ordering of the films. Suzuki and Gomyo show a very similar increase in band gap for Se-doped films grown with slightly smaller carrier concentrations. \cite{Suzuki} Because they see the effect for films with carrier concentrations lower than that at which the Burstein-Moss effect causes a shift in the "apparent" band gap, they conclude that this shift in the band gap is a manifestation of the extent of order.

The change from the ordered to the disordered state occurs at a smaller carrier concentration for films grown at 740°C than those at 670°C. Since the Burstein-Moss shift is unimportant for GaInP\(_2\) films doped at \( 3 \times 10^{18} \) cm\(^{-3} \) the interpretation of these results is more straightforward.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\( T_g \) (°C) & \( n \) (cm\(^{-3} \)) & \( E_g \) (eV) before Burstein-Moss correction & \( E_g \) (eV) after Burstein-Moss correction & Ordered Volume (\%)* \tabularnewline
\hline
670 & \( ~1 \times 10^{19} \) & 1.96 & \( 1.88 \pm 40 \) meV & weak \\
670 & \( 7 \times 10^{18} \) & 1.875 & \( 1.825 \pm 20 \) meV & medium \\
670 & \( 5 \times 10^{18} \) & 1.865 & \( 1.845 \pm 10 \) meV & medium \\
670* & \( 5 \times 10^{16} \) & 1.823 & \( 1.830 \pm 5 \) meV & medium \\
740 & \( 3 \times 10^{18} \) & 1.915 & \( 1.915 \pm 5 \) meV & disordered \\
740* & \( 2 \times 10^{18} \) & 1.885 & \( 1.885 \pm 5 \) meV & medium \\
740 & \( 4 \times 10^{16} \) & 1.880 & \( 1.880 \pm 5 \) meV & medium \\
600 & \( 2 \times 10^{19} \) & 1.96 & \( 1.9 \pm 60 \) meV & disordered \\
600 & \( 5 \times 10^{17} \) & 1.885 & \( 1.885 \pm 5 \) meV & very weak \\
600* & \( 2 \times 10^{16} \) & 1.880 & \( 1.88 \pm 5 \) meV & very weak \\
\hline
\end{tabular}
\caption{Table I}
\end{table}

*nominally undoped  
*measured from the dark-field superlattice images