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Evidence of Be₃P₂ formation during growth of Be-doped phosphorus-based semiconductor compounds

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In this work, we present evidence that Be_3P_2 microcrystals are formed in Be-doped phosphorus-based semiconductor compounds grown by chemical beam epitaxy. Our results suggest that microcrystal formation occurs when high Be concentrations ($>10^{18}$ cm^{-3}) and temperatures higher than 500 °C are used for crystal growth. The main consequence of Be_3P_2 formation is a high phosphorus consumption close to these microcrystals that causes a large density of P vacancies in the semiconductor layer. This results in reduced electrical mobility, lattice parameter reduction, and poor crystalinity of the film in general. © *1999 American Institute of Physics.* [S0003-6951(99)01624-1]

Beryllium is a commonly used shallow acceptor for III–V semiconductor layers grown by molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE) due to its high vapor pressure, close to unity sticking coefficient and low memory effects. However, for large concentrations, Be causes surface degradation[1,2] and, at least for phosphorus compounds, a small reduction in lattice parameter[3] as well as a reduction in the intensity and broadening of x-ray diffraction peak (rocking curve) measurements. In some cases, this effect is so large that it is not possible to consider the layer as crystalline. In these cases, we have measured Hall mobility as low as 5.0 cm²/V s or lower, at room temperature.

In this work, we present and discuss the effect of high Be concentration in the crystal quality of $In_xGa_{1-x}P$ layers lattice matched with GaAs ($x \sim 0.5$) grown by CBE. We have used phosphine, triethylgallium, and trimethylindium as phosphorus, gallium, and indium precursors, respectively. The growth temperature was varied in the range 500–540 °C. We have used solid Be in an effusion cell as the Be source, with cell temperature varied in the range 700–850 °C. Growth details will be given elsewhere.[4] Figure 1 shows the Hall carrier concentration as function of Be cell temperature for three growth temperatures: 500, 520, and 540 °C. This figure also shows the secondary ion mass spectrometry (SIMS) concentration measurements for the sample grown at 540 °C. We see that for samples grown at 520 and 540 °C, the carrier concentration saturates around 6×10^{18} and 3×10^{18} cm^{-3}, respectively, while for that grown at 500 °C, an exponential behavior is observed for all Be cell temperatures considered here. SIMS measurements show that actually the Be concentration does not saturate for the sample grown at 540 °C. The saturation occurs only for carrier (hole) concentration and is followed by surface degradation and electrical mobility reduction to the range 10–15 cm²/V s for higher Be concentration. For samples grown at 500 °C, we do not detect surface degradation by optical microscopy even for hole concentrations above 10^{19} cm^{-3}. Samples

grown at 500 °C present electrical mobilities about two (four) times greater than those of samples grown at 520 °C (540 °C) for the entire range of concentrations measured. It is worthwhile to mention that undoped samples grown at 540 °C are *n* type, present good morphologies and electrical mobility around 3000 cm²/V s. Figure 2 shows the x-ray diffraction measurements (XRD) for heavily Be-doped samples grown at different temperatures. For the growth at 500 °C, the mismatch observed is the same as the undoped sample, but the diffraction peak width increases slightly. For higher temperatures, however, we observe a reduction in the lattice parameter, which increases with Be concentration, as well a further increase in the diffraction peak width. Photoluminescence measurements (PL) were carried out at 77 K and were also used to evaluate alloy composition and crystal quality. The composition values calculated from PL and XRD agree very well for samples grown at 500 °C. For samples grown at 520 and 540 °C, however, the PL data indicate In-rich composition, while the XRD suggest a Ga-rich InGaP layer (In mole fraction varying from 0.51 to 0.475). This discrepancy between PL and XRD only occurs

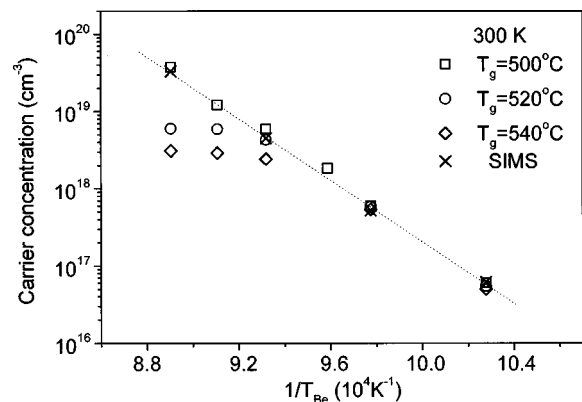FIG. 1. 300 K Hall carrier concentration against reciprocal of Be cell temperature for growth temperature of 500 °C (□), 520 °C (○), and 540 °C (◇). The dashed line is the linear fitting for SIMS measurements for the samples grown at 540 °C (×) and agrees well with the temperature dependence of Be vapor pressure.

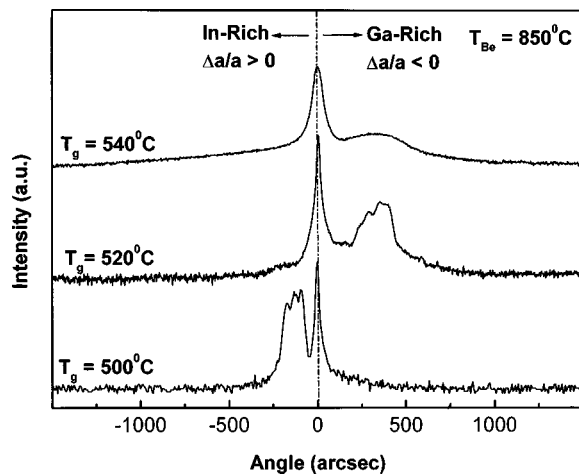[a]Corresponding author; electronic mail: mauro@ifi.unicamp.br

FIG. 2. Rocking curve for samples grown at three different temperatures: 500, 520, and 540 °C. The Be cell temperature was kept at 850 °C. InGaP layers are 2 μm thick.

FIG. 4. Rocking curve for samples grown at 540 °C with flows of 7.5 and 15 sccm of phosphine. The sample grown with 15 sccm is lattice matched with GaAs.

when high Be concentrations and temperatures are used for growth. A possible interpretation for this result comes from the fact that the presence of crystal defects in the layer could affect the XRD data with no significant change in the PL peak energy. The PL intensity and linewidth, on the other hand, should change more noticeably at first if the layer presents a poor crystal quality.

In this sense, the PL emission of the heavily doped samples (Fig. 3) presents a drop in intensity and an increase in linewidth with increasing growth temperature, as well the reduction in lattice parameter observed in the XRD. A similar behavior was observed for the XRD of heavily Be-doped InP samples.[3] In that work, the difference between the atomic radii of Be and In was considered as the cause of the compression. For the mismatch values and Be concentrations considered here, however, this explanation does not seem realistic. The formation of complexes involving Be and P, and the consequent creation of P vacancies in the layer should be considered as well. The presence of such defects in the layer should not alter the alloy composition and could create the average lattice parameter reduction observed in the broad XRD peaks for heavily doped layers grown at higher temperatures.
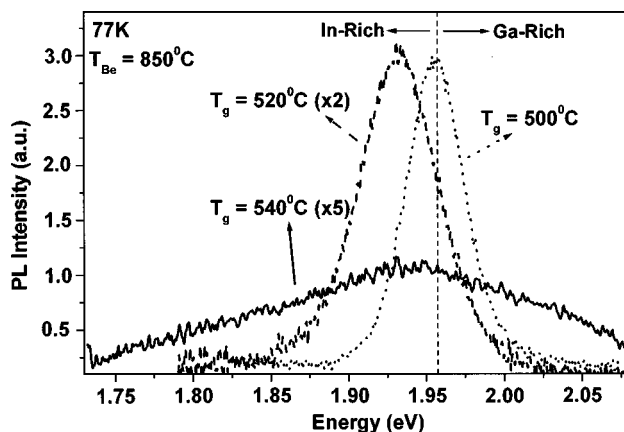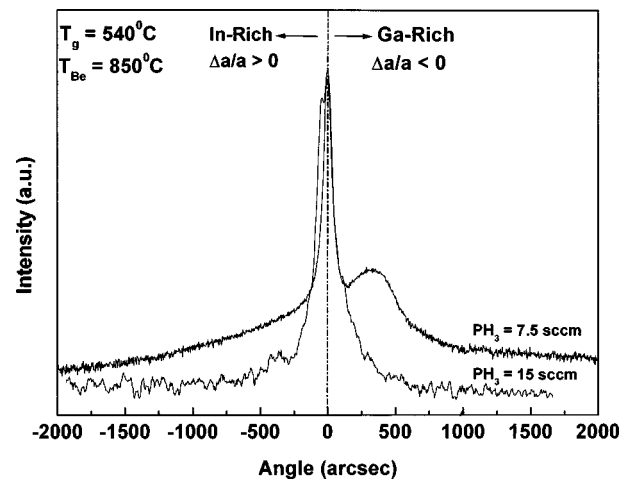
Stackelberg and Paulus[5] have obtained Be_3P_2 passing

P-charged H_2 gas over Be at 700 °C. Be_3P_2 was also obtained by El Maslout *et al.*[6] by direct reaction of P vapor with Be at 700 °C. Since we have both P and Be at high temperature, the Be_3P_2 formation during growth, already suggested by Panish *et al.*[7] should not be neglected. Since Be diffusion on the surface is a thermally activated process and increases exponentially with temperature, the probability of Be and P atoms repeated interactions should increase with temperature as well. Moreover, the higher the temperature used for growth, the closer it gets to the temperature region where Be_3P_2 formation has indeed been observed.[6] Therefore, we should expect a higher rate of Be_3P_2 formation when the growth temperature is increased.

The Be_3P_2 structure is cubic bixbyite and its unit cell contains 16 molecules.[8] The lattice parameter is 1.015 nm. If microcrystals of Be_3P_2 are formed during growth, a large quantity of phosphorus will be consumed in this process (the Be_3P_2 unit cell contains 32 phosphorus atoms). Therefore, if excess P is not used during growth, we can expect a large density of P vacancies in the InGaP (or InP) layer. This can reduce the lattice parameter and even degrade the crystal quality of the layer.

In order to verify this hypothesis, we have grown a Be-

FIG. 3. 77 K PL spectra for heavily Be-doped samples grown at different temperatures (same as in Fig. 2).
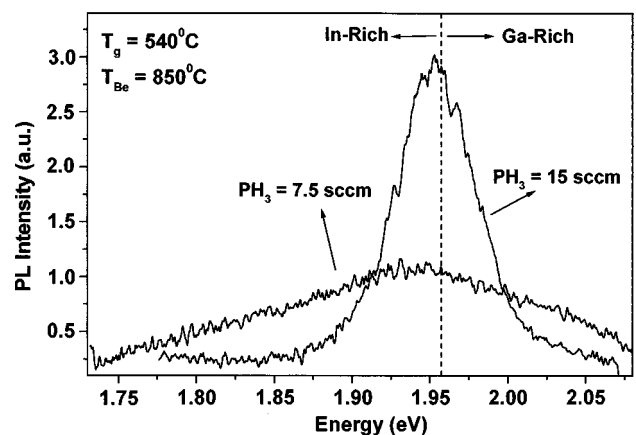

FIG. 5. 77 K PL spectra for samples grown at the same Be cell and growth temperatures. The phosphine flows are 7.5 and 15 sccm, as indicated in the figure.

doped layer of $In_xGa_{1-x}P$ in the conditions favoring a large formation of defects according to our interpretation of the XRD data (growth temperature of 540 °C and Be cell temperature at 850 °C) (see Fig. 4) but with phosphine flow doubled. The morphology for this sample is mirror-like in the optical microscope and the changes in XRD and PL data can be observed in Figs. 4 and 5, respectively. The alloy composition values calculated from PL and XRD agree with each other and the crystal quality was greatly improved as we can observe from the PL and XRD linewidths. However, no improvements in electrical mobility were observed for the sample grown under a larger PH_3 flow. This was expected since increasing the P overpressure should not affect the Be_3P_2 formation rate but only supply P for the vacancies.

In summary, we propose that during growth of heavily Be-doped phosphorus compounds, Be_3P_2 microcrystals are formed consuming a large quantity of P and consequently causing a large density of P vacancies in the film. This process is responsible for a reduction in the lattice parameter measured by XRD and degradation of crystal quality. Although this work deals only with phosphorus compounds, we believe that the surface degradation[9,10] of heavily Be-doped arsenic compounds may have the same origin (Be_3As_2, in this case).

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