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GaP films, epitaxially grown at a low temperature (LT) of ~200 °C by gas source molecular beam epitaxy, were reported recently to have excess phosphorus. In this letter, we report on the quantitative determination of the excess phosphorus in the LT films, using various approaches. Analytical scanning transmission electron microscopy, double-crystal x-ray diffraction, and particle-induced x-ray emission showed that the LT GaP films incorporated excess phosphorus of ~0.6–2 at. %. The amount of excess phosphorus estimated from Raman scattering measurements, using the LO-TO phonon frequency splitting data of the as-grown LT GaP and bulk GaP, was in general agreement with those obtained from other techniques.

GaAs grown at a low temperature (LT) of ~200 °C by molecular beam epitaxy (MBE) and then annealed at high temperatures has been found to be semi-insulating. It exhibited several applications in GaAs devices.[1,2] Excess arsenic on the order of 1 at. % was found to be incorporated during the LT growth.[3] Recently, the preliminary studies on LT GaP[4] and InGaP[5] also revealed the presence of excess phosphorus in the epilayers, and the as-grown and annealed samples exhibited semi-insulating properties. The semi-insulating nature of LT GaP and InGaP was proposed to be mainly a result of excess-phosphorus-related deep levels. In this letter, we report on the quantitative determination of the nonstoichiometry of LT GaP grown at ~200 °C. Several characterization techniques were used such as analytical scanning transmission electron microscopy (STEM), double-crystal x-ray diffraction (DCXRD), particle-induced x-ray emission (PIXE), and Raman scattering.

LT GaP epilayers were grown using a Riber 32RD gas source molecular beam epitaxy (GSMBE) system. Solid Ga and 100% PH_3 precracked at 950 °C were used as III-V sources. The growth rate was 1 μm/h and all the samples used in this work had a mirrorlike morphology. GaP substrate was used as a reference for all characterizations in this work. More detailed experimental conditions were reported earlier.[4]

Analytical STEM was performed in a TOPCON EM-002B ultra-high-resolution analytical electron microscope equipped with an electron probe. The TEM facility was operated at 120 kV with the probe diameter set at 4.9 nm. The nonstoichiometry of the LT material was also evaluated using PIXE technique in the University of California at Berkeley. The measurements were performed by employing a 0.5 MeV H^+ ion beam with samples tilted at 65° with respect to the ion beam. Raman scattering measurements were carried out in backscatter configuration at room temperature using the 514.5 nm line of an Ar^+ ion laser. The laser power was 250 mW, and the spot size was ~2 mm×80 μm obtained using a cylindrical lens. Both laser power and laser spot size were kept constant from run to run for the consistency of the experiment.

Excess phosphorus in LT GaP films were determined by using the analytical STEM technique. This technique measures phosphorus and gallium x-ray signals, the $K\alpha$ signals of which are used to get the [P]/[Ga] atomic ratio. The excess phosphorus is defined as ([P]−[Ga])/([P]+[Ga]) similar to the calculation of excess arsenic in LT GaAs.[6] In order for the analysis to be statistically accurate, about ten data points were taken by setting the electron probe at different locations within the same layer. The averaged atomic ratio would be useful for the excess phosphorus calculation. As an example, the LT film grown at 190 °C showed the normalized [P]/[Ga] atomic ratios ranging from 1.0189 to 1.0346. The average atomic ratio is 1.0243, which is equivalent to an excess phosphorus amount of 1.20 at. %. With the same approach, the STEM analyses on the LT films grown at 180 and 200 °C yielded 1.47 and 0.73 at. % excess phosphorus, respectively.

DCXRD analyses revealed that the excess phosphorus atoms incorporated into LT GaP caused a lattice expansion with respect to bulk GaP, manifested by the Bragg angle splitting. Shown in Fig. 1 is a typical rocking curve of (113) reflections obtained on the unannealed sample grown at 180 °C. The epilayer peak at lower Bragg angle position has a splitting of 220 arc sec from the substrate peak. For the simplicity of the excess phosphorus calculation from the

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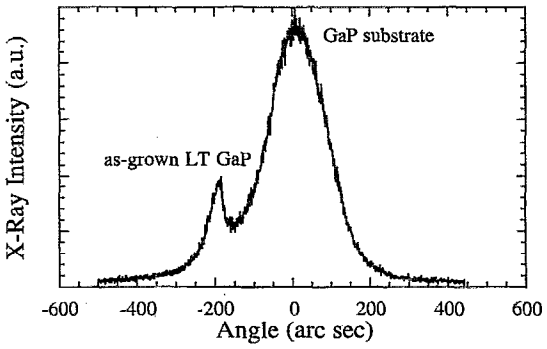

FIG. 1. Double-crystal x-ray diffraction from (113) reflection planes of the unannealed LT GaP sample grown at 180 °C.

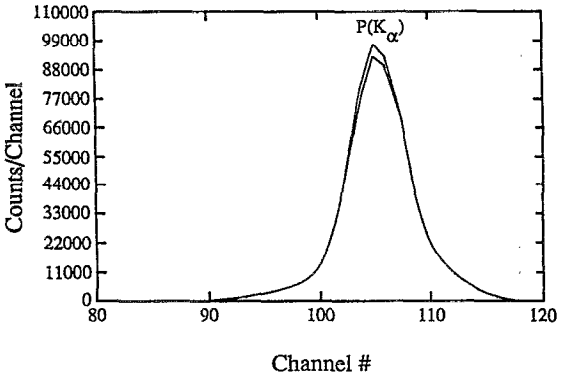

FIG. 2. 0.5 MeV H^+ PIXE superimposed P($K\alpha$) x-ray signals from the as-grown LT GaP epilayer grown at ~160 °C (top) and GaP substrate (bottom). Note that the difference in intensity of the two spectra indicates a higher excess phosphorus content in the LT GaP epilayer.

splitting, two assumptions have been made. First, the lattice is assumed to be uniformly and elastically expanded, that is, the LT GaP still has a cubic lattice. This assumption, although not exact, can be considered as an approximation. Second, the excess phosphorus is incorporated as misfitting particles (both as interstitials and antisites). Let ϵ be the elastic strain of the LT GaP lattice, and δ the net lattice mismatch (strain effect corrected) between the LT GaP and bulk GaP lattices. Then, the two parameters ϵ and δ can be related by the Bullough and Newman equation:[7]

$$\epsilon = \frac{\delta(1+\nu)}{3(1-\nu)}, \tag{1}$$

where ν is Poisson's ratio. Note that ν is about 1/3 for almost all III-V semiconductors. Therefore, the ϵ-δ relation can be simplified as

$$\epsilon \approx \frac{2}{3}\delta. \tag{2}$$

Now, let δ_m denote the measured lattice mismatch (strain effect included) between the LT GaP and bulk GaP lattices. In theory, it is composed of the elastic strain and net lattice mismatch, i.e.,

$$\delta_m = \epsilon + \delta. \tag{3}$$

Substituting Eq. (2) into Eq. (3) and solving for δ gives the following approximate relation between δ and δ_m:

$$\delta \approx \frac{3}{5}\delta_m. \tag{4}$$

Let a_e be the lattice constant of LT GaP for which the elastic strain effect is corrected according to Eq. (4), and let a_s be the lattice constant of bulk GaP. Then the net volume increase of a unit cell of the LT GaP lattice can be calculated by $\Delta V = a_e^3 - a_s^3$. Considering a phosphorus atom as a hard sphere with a radius of 1.23 Å,[8] and that there are four phosphorus atoms in a unit cell of a stoichiometric GaP, one can now calculate the percentage of excess phosphorus incorporated in ΔV. Such calculation yielded 1.89 at. % excess phosphorus in the film grown at 180 °C. DCXRD also showed that the films grown at 190 and 200 °C had splittings of −230 and −70 arc sec, respectively. The amounts of excess phosphorus causing the splittings were calculated to be 1.97 and 0.60 at. %, respectively. As expected, this approach of nonstoichiometry determination using DCXRD is convenient and it gives a relatively reasonable estimation.

The PIXE technique also measures the [P]/[Ga] atomic ratios using $K\alpha$ x rays. The overall statistical error of this technique on the measurement of the atomic ratios was estimated to be about 0.4%. A [P]/[Ga] ratio of 1.025 was obtained for the LT GaP film grown at 190 °C, indicating the excess phosphorus of 1.23 at. %. This value is in good agreement with that obtained from the same sample by the STEM technique. The PIXE measurements made on the LT film grown at a lower temperature of ~160 °C yielded a [P]/[Ga] ratio of 1.045, corresponding to the excess phosphorus of 2.2 at. %. Shown in Fig. 2 is the superimposed P($K\alpha$) x-ray signals of that sample (top) and GaP substrate (bottom). Both spectra were obtained under identical conditions. The intensity difference of the two spectra shown in Fig. 2 indicates a higher phosphorus content in the LT GaP sample. The Ga($K\alpha$) x-ray signals of the sample and the substrate were totally overlapped and thus not shown here. Note that this sample showed high dislocation density by TEM, but was still crystalline as determined by electron diffraction pattern.

Raman scattering measurements were performed on the as-grown, annealed LT GaP, and bulk GaP under identical

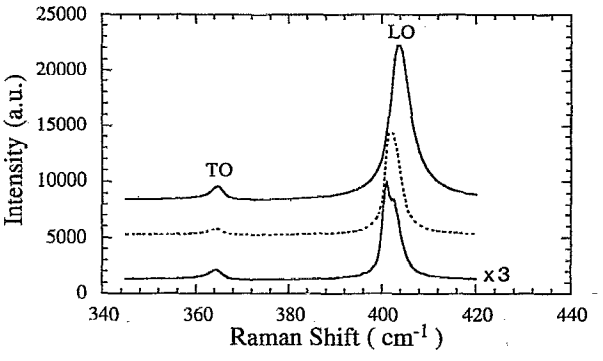

FIG. 3. Raman spectra of bulk GaP (top), annealed LT GaP (middle), and as-grown LT GaP (bottom).

TABLE I. LO and TO phonon peak frequencies of the Raman spectra in Fig. 3. The resolution of these measurements is about ± 0.4 cm^{-1}.

Sample	TO frequency	LO frequency
Bulk GaP	364.8	403.8
Annealed LT GaP	364.6	402.0
As-grown LT GaP	364.4	401.6

conditions. Shown in Fig. 3 are the Raman spectra of the as-grown, annealed (at 700 °C for 1 h) LT GaP, and bulk GaP. The TO phonons of the three samples have much weaker intensities since they are not allowed in the (100) orientation. More significantly, they do not show any substantial frequency shift. The LO phonons of the as-grown sample, however, shift down in frequency from the bulk material by 2.2 cm^{-1}. The frequency of the annealed sample showed a small shift from that of the as-grown sample within margin of the resolution error, indicating a negligible effect of annealing on the frequency. The peak frequencies for the spectra in Fig. 3 are listed in Table I. The reduction of LO-TO splitting of the as-grown LT GaP with respect to that of the bulk GaP may mainly be a result of the reduction in the effective charge for P_{Ga} antisite defects by analogy with the similar study of LT GaAs.[9] Hence, the excess phosphorus incorporated in LT GaP as antisites can be correlated to the LO-TO splitting by following the similar approach proposed for LT GaAs. Let x denote a fraction of P, substituting Ga, implying a nonstoichiometry of $Ga_{1-x}P_{1+x}$, $\mu(x)$ the average value of the reduced mass of the unit cell due to the fraction x of P_{Ga} antisites, and $q(x)$ the average value of the effective charge on the ions. Then we have

$$\mu(x)=(1-0.3848x)\mu_{\mathrm{GaP}} \tag{5}$$

with the values 69.72 and 30.97376 amu for the masses of Ga and P, respectively, and

$$q(x)=(1-x)q_{\mathrm{GaP}}. \tag{6}$$

Therefore, the LO-TO splitting as a function of x can be expressed as

$$\frac{[\omega_L^2-\omega_T^2]_{\mathrm{Ga}_{1-x}\mathrm{P}_{1+x}}}{[\omega_L^2-\omega_T^2]_{\mathrm{GaP}}}=\frac{(1-x)^2}{(1-0.3848x)}, \tag{7}$$

where ω_L and ω_T are the LO and TO phonon frequencies, respectively. Substituting the frequencies listed in Table I for the as-grown LT GaP and bulk GaP samples into the above equation and solving for x, we get $x\sim 0.03$. The resolution of the Raman measurements on phonon frequencies is about ± 0.4 cm^{-1} and this error in frequency can produce an error of approximately ± 0.01 in x. The value of x is fairly close to those results obtained from STEM and PIXE if the lower limit is considered.

TABLE II. Excess phosphorus in LT GaP grown at various temperatures (T_s). The values of stoichiometry were determined by STEM and DCXRD techniques.

T_s (°C)	STEM (at. %)	DCXRD (at. %)
180	1.47	1.89
190	1.20	1.97
200	0.73	0.60

In conclusion, LT GaP films grown at 180–200 °C by GSMBE exhibit a quantity of excess phosphorus ranging from ~0.6 to 2 at. %. The excess phosphorus determined by the different approaches discussed above (namely, STEM, DCXRD, PIXE and Raman scattering) are in general agreement. The values of excess phosphorus vs growth temperature determined by STEM and DCXRD are tabulated in Table II. As a whole, the quantity of excess phosphorus appeared to vary inversely with growth temperature. At this point, a question may be raised about how the excess phosphorus is incorporated in the crystal lattice. Raman measurements showed the reduction of LO-TO splitting for the as-grown LT GaP, implying the existence of P_{Ga} antisite defects. DCXRD indicated a lattice expansion, suggesting that the excess phosphorus may be incorporated also as interstitials. Since x-ray measures the change in lattice constant, which may be caused by both interstitials and antisites, we conclude that both defects exist in the lattice. Therefore, more analyses are needed about where this excess phosphorus is and how annealing that, we know, causes some segregations can affect these results.

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