Thermodynamic analysis has been applied to the vapor over a ZnGeP$_2$ crystal when the chlorine source is provided by ZnCl$_2$. ZnGeP$_2$ film growth has been examined and the electrophysical and photoluminescence parameters have been measured. All these autoepitaxial films have the chalcopyrite structure, while those parameters are determined by the defects and the substrate orientation.

Heteroepitaxy in a closed gas-transport system produces ZnGeP$_2$-2GaP solid solutions on gallium phosphide substrates when the source is ZnGeP$_2$, and the composition varies regularly over the thickness. No previous study has been made on gas-phase homoepitaxy for zinc germanium diphosphide. We have examined the preparation conditions and properties for homoepitaxial ZnGeP$_2$ films grown on substrates with various orientations in a closed system, with ZnCl$_2$ as transport agent.

Proper growth condition choice has been based on thermodynamic analysis of the vapor composition in the ZnGeP$_2$-ZnCl$_2$ system at various temperatures; it was assumed that the vapor consisted of GeCl, GeCl$_2$, GeCl$_4$, Zn, ZnCl, ZnCl$_2$, P, P$_2$, P$_4$, PCl, PCl$_3$, PCl$_5$, Cl, Cl$_2$. We considered a set of independent reactions and calculated the equilibrium constants. The thermal constants were taken from [4]. We found that the vapor at 873-1273 K consists mainly of ZnCl$_2$, Zn, GeCl$_2$, P$_2$, P$_4$, the other components having molar concentrations lower by four or five orders of magnitude.

ZnGeP$_2$ is transported dissociatively, i.e., the zinc is transported in atomic form, while the phosphorus and germanium are as P$_2$, P$_4$, and GeCl$_2$ correspondingly, with the crystal growing via the overall reaction:

$$2\text{Zn (g)} + \text{P}_2 (g) + \text{GeCl}_2 (g) \rightleftharpoons \text{ZnGeP}_2 (s) + \text{ZnCl}_2 (g).$$

The performance of the ZnCl$_2$ is defined as the ratio of the ZnGeP$_2$ gram moles to the Cl gram atoms and increases over the range 600-1273 K but decreases as the ZnCl$_2$ concentration rises from 0.01 to 1 mg/cm$^3$.

The calculations indicated the following states for ZnGeP$_2$ homoepitaxy in a two-temperature closed gas system: temperatures in the source and substrate zones 1233 and 1173 K correspondingly, ZnCl$_2$ concentration 1 mg/cm$^3$, growth time 3 h.

The films were grown in a silica tube evacuated to 10$^{-2}$ Pa; the substrates and sources were provided by a high-resistance ZnGeP$_2$ single crystal grown by Bridgman's method.

We used substrates with (100), (001), (112) orientations, which were mechanically polished and were then gas-etched at 1213 K for 10 min immediately before use.

The first tests showed that polycrystalline films containing separate large crystals grew on (112); (100) and (001) gave regions containing single-crystal material, which alternated with polycrystalline ones. This means that the vapor composition here causes difficulties for epitaxial growth, which are not eliminated by altering the source and substrate temperatures or the transport-agent concentration. The difficulties may be due to stoichiometry deviations (relative to the source) in the vapor as regards phosphorus because ZnCl$_2$ is used. This was tested by adding phosphorus (1 mg/cm$^3$) to the tube, which influenced the growth considerably. All the substrate orientations gave single-crystal layers growing at an average rate of 6-7 μm/h. The morphology and the growth figures differed with the orientation; (100) and (001) gave mirror-smooth films containing large growth figures, which resembled those characteristic of those orientations in cubic crystals [5]. The (112) sub-
TABLE 1

<table>
<thead>
<tr>
<th>Substrate orientation</th>
<th>Carrier concentration, cm(^{-3})</th>
<th>Mobility, cm(^2)/V·sec</th>
<th>Ionization energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>1-3×10(^{13})</td>
<td>10-30</td>
<td>0.12</td>
</tr>
<tr>
<td>(100)</td>
<td>6-9×10(^{15})</td>
<td>3-10</td>
<td>0.1</td>
</tr>
<tr>
<td>(112)</td>
<td>5-8×10(^{17})</td>
<td>2-8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Fig. 1

Fig. 1. Temperature dependence of molar concentrations in the ZnGeP\(_2\)-ZnCl\(_2\) system for an initial chlorine concentration of 1 mg/cm\(^3\).

Fig. 2

Fig. 2. 77 K ZnGeP\(_2\) photoluminescence spectra: 1) (001) substrate orientation, hole concentration 2×10\(^{15}\) cm\(^{-3}\); 2) (112), 6×10\(^{17}\) cm\(^{-3}\).

...substrates gave truncated pyramids elongated in one direction. The epitaxial films on those substrates were very inhomogeneous over the thickness, which was found to be due to selective gas etching before the growth.

The large growth figures were always accompanied by small growth pits with linear dimensions 1-3 μm and concentrations up to 10\(^8\)-10\(^9\) cm\(^{-2}\).

X-ray structure measurements showed that the films had the chalcopyrite structure (\(\overline{1}42d\)); microprobe analysis showed the composition Zn:Ge:P = 32.8:36.6:30.6 mass %, which corresponds to about 0.4 mass % phosphorus deficiency from stoichiometry. That composition differs from stoichiometric by not more than 10\(^{-4}\) atomic proportion in the homogeneity range [6], so the excess Zn (about 0.1 mass %) and Ge (about 0.3 mass %) must be present as microscopic inclusions of a second phase acting as nucleation centers for the small growth pits.

We measured the photoluminescence spectra and the temperature dependence for the conductivity and Hall constant for these ZnGeP\(_2\) films; they were all p-type, with properties dependent on the substrate orientation. Table 1 gives typical parameters.

A ZnGeP\(_2\) crystal having a carrier concentration of 10\(^{15}\)-10\(^{17}\) cm\(^{-3}\) can be made by Ga doping [7], Cu doping [8], heat treatment in zinc vapor [9], and recrystallization in a gas-transport system with ZnCl\(_2\) as agent [10]. Shallow acceptor centers (\(E_A = 0.1\) eV) in ZnGeP\(_2\) are [9] provided by zinc vacancies (\(V_{Zn}\)) and zinc atoms at phosphorus nodes (\(ZnP\)).

These films have properties similar to those of the crystals in [8-10], so one assumes that the conductivity in the main is determined by disordering defects of \(ZnP\) type on account of the excess zinc. On the other hand, one cannot exclude doping by some uncontrolled (background) impurity such as copper or oxygen, which may interact with the defects to give complexes.

The carrier concentration is dependent on the substrate orientation because of growth anisotropy influencing the defect formation; the comparatively small hole mobilities and the large differences from one specimen to another are due to the marked compensation and to the zinc and germanium inclusions, whose concentrations are very much dependent on the growth conditions.