JOURNAL OF SOLID STATE CHEMISTRY 95, 346–351 (1991)

Studies on the Electrical Properties of Rare Earth Monophosphides

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Received January 17, 1991; in revised form July 8, 1991

The rare earth monophosphides *Ln*P (*Ln* = La, Nd Sm, and Y) have been prepared. Their electrical properties have been studied. The compounds exhibit a lower resistivity and higher carrier concentration. Evidence that shows semiconducting properties has been obtained from the study of energy gaps and the negative temperature coefficient of resistance. Their energy gaps are in the range of 1.0–1.46 eV. The electrical properties of *Ln*P can be reasonably well explained by the proposed band scheme.

Introduction

Since the conventional IIIA–VA compound semiconductors such as GaAs, GaP, etc., are widely used in microwave, Hall, photoelectric, and infrared detection devices, many research groups have investigated compounds of group IIIB, Sc, Y, and lathanides and group VA. There is considerable research on rare earth nitrides and arsenides but fewer studies on rare earth phosphides. The investigation for rare earth phosphides was focused mainly on the preparation and structure (*1–4*). Hiscocks and Mullin (*5*) and Yim *et al.* (*6*) reported the energy gaps of 1.09 eV and 1.1 eV for SmP and ScP obtained from the absorption spectrum of thin films. Kaldis *et al.* (*7*) and Güntherodt and Wachter (*8*) measured the reflection spectrum of a small crystal of GdP. Its electric structure was analyzed by means of the Kramers–Kronig relation. The $4f^7$ level of Gd^{3+} is positioned about 7 eV below the Fermi level, and the valence band is formed by the $3p^6$ states of phosphorus, while the conduction band is formed by $5d6s$ states of gadolinium. The difference between the top of the valence band (E_V) and the Fermi level (E_F) amounts to 0.65 eV. It is possible to predict, theoretically, the energy gap of new compounds by extrapolating or interpolating empirical models based on established data from known compounds. Sclar (*9*) and Yang Ping and Guao Xiaohui (*10*) reported that the energy gaps of *Ln*P were about 1.0 eV as determined by an empirical formula. Hasegawa and Yanase (*11*) reported that the valence band and conduction band of GdP overlap, on the basis of energy band calculations by means of the APW method. Research on the other properties of *Ln*P has not been reported in the literature.

In this paper we report on the absorption spectrum and electrical properties of rare earth monophosphides. Their energy gaps are about 1.0–1.46 eV. The compounds exhibit the negative temperature coefficient of resistance. *Ln*P is a semiconductor with higher carrier concentrations.

0022-4596/91 $3.00

Experimental

Rare earth filings of 99.9% purity and red phosphorus of 99.99% purity were sealed in an evacuated quartz ampoule under a pressure of 6.6×10^{-3} Pa in *AB* form. It was placed into a furnace and heated at 1100°C for 20 hr. This reaction, in practice, is very dangerous. Since the vapor pressure of phosphorus is high at high temperature, to prevent a violent explosion the rate of raising the temperature from 300 to 1100°C must be less than 1°C/min. The black powder was reground and pressed into pellets. The pellets were sealed again in an evacuated silica tube under a pressure of 6.6×10^{-3} Pa and sintered at 1100°C for 10 hr.

The thin films of *Ln*P were deposited on an optical glass substrate under a pressure of 6.6×10^{-3} Pa in a GD-450B vacuum coating apparatus.

The structure of LnP was analyzed by a Regaku Denki 2028 D/max-IIB X-ray powder diffractometer. The absorption spectrum was measured by a Zeiss, VSU_2 – p spectrophotometer in the range of 300–2100 nm. The electric conduction type was measured by a hot-probe. The resistivities and Hall coefficient were measured by a four-probe and Hall effect apparatus.

Results

(*1*) *Structure of LnP*

The X-ray powder diffraction results of LaP, NdP, and SmP are in accord with the standard JCPDS cards. This shows that all three *Ln*P samples prepared by the element synthesis method are cubic. The XRD spectrum of YP was indexed and its lattice parameter was calculated because no JCPDS card for YP has been issued. The results are given in Table I. It is shown that YP is also a cubic phase with a lattice parameter a = 0.5652 nm.

TABLE I

THE X-RAY DIFFRACTION DATA OF YP

			d (nm)		
h	k	l	Experimental	Calculated	I/I_0
1	1	1	0.3257	0.3263	45
2	0	0	0.2823	0.2826	100
2	2	0	0.1998	0.1998	65
3	1	1	0.1704	0.1704	20
2	2	2	0.1631	0.1632	20
4	0	0	0.1414	0.1413	10
3	3	1	0.1304	0.1297	5
4	2	0	0.1265	0.1264	25
4	2	2	0.1158	0.1154	20
3	3	3	0.1092	0.1089	5

(*2*) *Optical Properties of LnP*

The absorption spectra obtained on *Ln*P are shown in Fig. 1.

No characteristic peaks produced by the *f–f* electron transition of the rare earths appear in the curves. All absorption curves show a continuous transition between the electronic bands of the compounds. These curves are similar to those of the allowed direct transition of IIIA–VA semiconductors. According to the current theory of photon absorption in solids, the absorption coefficient (μ) depends on the photon energy ($h\nu$): the photon energy is approximately equal to the energy gaps (Eg) in the region of the band edge. So, we may write (*5*): $= A(h\nu - \mathrm{Eg})^2$; the absorption coefficient in a solid is given by $I/I_0 = e^{-\mu d}$, where d is the sample thickness. Therefore, we obtain: $(\ln(I_0/I))^2 = (Ad)^2 (h\nu - \mathrm{Eg})$. An extrapolation of the linear portion of the curves to $(\ln(I_0/I))^2 = 0$ was used to determine Eg. The results are given in Table II.

Although the measured values differ from the predictions of Sclar (*9*) and Yang Ping and Guao Xiaohui (*10*), the basic prediction that *Ln*P should show semiconducting characteristics is borne out. The Eg value for SmP is in accord with the result of Hiscocks and Mullin (*5*).

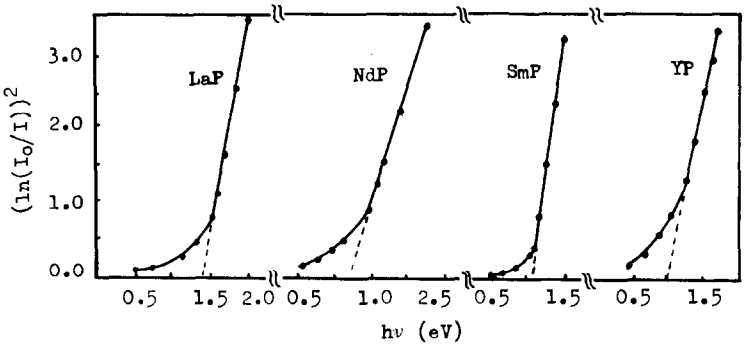

FIG. 1. The absorption spectra of *Ln*P.

(3) *Electrical Properties of LnP*

The results of electrical properties measured are shown in Table II. It is evident that *Ln*P has a low resistivity and high carrier concentration at room temperature. The Hall coefficient is negative; the electric conduction is n-type. The important behavior of semiconductors is the negative temperature coefficient of resistance and the rectifying effect. The resistance dependence of temperature was measured from 77 to 300 K. The results are shown in Fig. 2.

It is evident that the resistance of *Ln*P gradually falls with increasing temperature. The compounds exhibit a negative temperature coefficient of resistance, indicating semiconducting behavior. According to the relationship between temperature and resistance of *Ln*P, the activation energy (ΔE) and the difference between the bottom of the conduction band and the Fermi level ($E_C - E_F$) have been calculated by the least-squares method. These values are also given in Table II. It is seen that the activation energy of *Ln*P is very small. This suggests that the Fermi level is very close to the con-

TABLE II

THE PROPERTIES OF *Ln*P

Compounds	LaP	NdP	SmP	YP
Lattice parameters (nm) ± 0.02%	0.6025	0.5826	0.5760	0.5652
Energy gaps (Eg, eV)	1.46 ± 2%	1.15 ± 2%	1.10 ± 2%	1.00 ± 2%
Resistivity (ohm-cm) ± 0.2%	3.7×10^{-2}	6.2×10^{-2}	1.0×10^{-2}	5.6×10^{-2}
Electric cond. type	n	n	n	n
Hall coefficient (cm^3/C)	−14.80 ± 2%	—	−1.94 ± 2%	−11.40 ± 2%
Carrier concentration (cm^{-3})	$4.2 \pm 0.1 \times 10^{17}$	—	$3.2 \pm 0.1 \times 10^{18}$	$5.5 \pm 0.1 \times 10^{17}$
Hall mobility (μ_H, $cm^2/V.S$)	400 ± 2	—	194 ± 2	204 ± 2
Activation energy (ΔE, eV) ± 0.1 × 10^n	1.4×10^{-1} 283–353 K	6.3×10^{-3} 93–233 K	3.6×10^{-3} 85–193 K 1.2×10^{-2} 193–228 K	1.8×10^{-2} 116–148 K 1.1×10^{-2} 163–308 K
Difference between conduction band edge and Fermi level $E_C - E_F$ (eV) ± 0.1 × 10^n	7.2×10^{-2}	3.3×10^{-3}	6.0×10^{-3}	5.3×10^{-3}

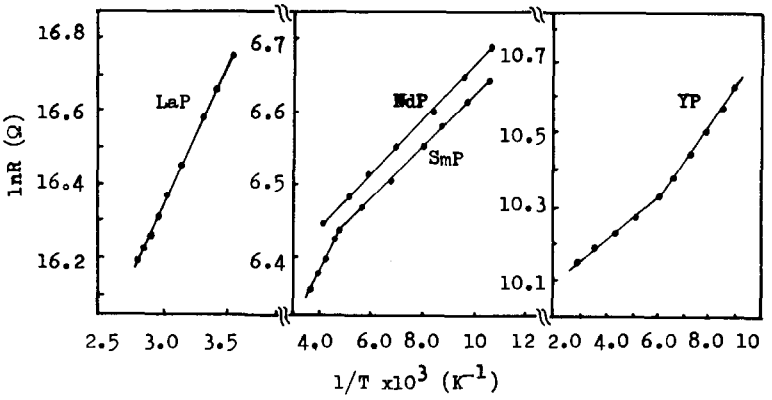

FIG. 2. The relationship between temperature and resistance of *Ln*P.

duction band. Thus, *Ln*P has a higher carrier concentration and lower resistivity. The fact that *Ln*P has smaller activation energy is evidently due to extrinsic, rather than intrinsic, effects. An extrinsic effect may be caused by a lattice defect or by impurities introduced in the high temperature preparation. It is one reason that rare earth elements have a specific active property.

(4) Rectifying Characteristic of LnP

In order to determine whether *Ln*P can form a p–n junction with p–Si as in conventional semiconductors, *Ln*P was deposited on a polished p–Si substrate under a pressure of 6.6×10^{-3} Pa. The Al–Ag back electrode was deposited on a p–Si substrate and the Al–Ag grid electrode was deposited on the *Ln*P thin films. A typical I–V characteristic curve of YP/Si is recorded in Fig. 3.

It is shown that as a positive bias of 0.74 V was applied across YP/Si a forward current of 9.9 mA was obtained; when a negative bias was −0.72 V, the backward current was −0.42 mA. The marked rectifying characteristic proves that a p–n junction has been formed on the YP/Si.

Discussion

The electron configuration $5d^16s^2$ or $4f^n5d^06s^2$ is the same for all rare earth elements. Because the orbit radius of the rare earth elements is larger, the binding force of atomic cores atracting outer-shell electrons is weaker. When the rare earth elements react to phosphorus, their three valence electrons are very easy to excite into the 3*p* orbits of phosphorus. Therefore, the conduction band of *Ln*P is made up of empty 5*d*6*s* orbits of the rare earth elements. The *d* orbits, on the other hand, are split into two subbands, d_{e_g} and $d_{t_{2g}}$. The valence band of *Ln*P is formed by the filled 3*p* orbits of phosphorus. The Fermi level is taken as the zero of energy in the energy band scheme. The relative position of conduction bands can be determined by the $E_C - E_F$ values in

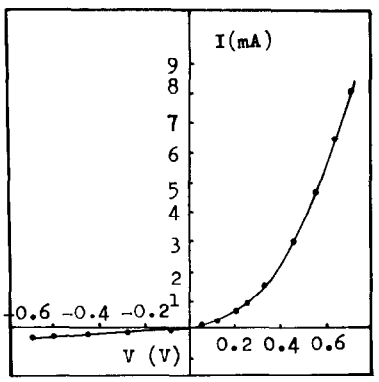

FIG. 3. The I–V characteristic curve of YP/Si.

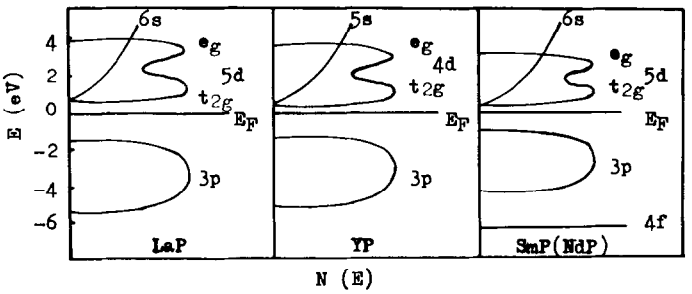

FIG. 4. The energy band patterns of *Ln*P.

Table II. The relative position between the valence band and conduction band can be determined by the energy gaps of *Ln*P. The energy band patterns of LaP and YP based on these considerations are drawn in Fig. 3. NdP and SmP have a similar band pattern but the position of the 4*f* level is not the same. The position of the 4*f* level can be estimated by comparison with the results for GdP. The 4*f* orbit of Gd^{3+} is a complete half-filled, i.e., $4f^7$, and the orbital energy is therefore lower. The 4*f* orbit of Gd^{3+} is localized roughly 7 eV below the Fermi level (*12*). The 4*f* level of Nd^{3+} and Sm^{3+} is $4f^3$ and $4f^5$, respectively. Their orbital energies are higher than these of Gd^{3+} because of the spin interaction. Since the spin interaction belongs to the weak interaction, we infer that the 4*f* levels are also localized about 6–7 eV below the Fermi level. The energy band patterns of NdP and SmP based on these considerations are drawn in Fig. 4.

The optical and electrical properties of *Ln*P can be reasonably well explained by the energy band patterns above. When light with a photon energy greater than 1.46 eV is incident on *Ln*P, a sharp band transition is exhibited by the absorption spectra. The 4*f* electrons of *Ln*P are localized roughly 6–7 eV below the Fermi level; thus, they do not participate in the optical and electrical action. The sharp transition involves the action between outer-shell electrons. The Fermi level is so close to the conduction band that *Ln*P exhibits not only a small activation energy but also a high carrier concentration and a low resistivity. Since *Ln*P compounds have very high melting points, they may have important device applications.

Conclusions

The optical properties of *Ln*P have been investigated by the absorption spectra of thin films. They show a direction band transition of a semiconductor. Their energy gaps examined are in the range of 1.0–1.46 eV. Their resistivities are low, falling in the range of 10^{-2} ohm-cm and their Hall coefficients are negative, indicating n-type electric conduction. Two important characteristics, the negative temperature coefficient of resistance and the rectifying effect, are taken as evidence that *Ln*P is a semiconductor. Their optical and electrical properties can be fairly explained by the possible band patterns. Rare earth monophosphides may have potential usefulness as device materials.

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