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INVESTIGATION OF THE PHOTOELECTRONIC PROPERTIES OF RARE EARTH MONOPHOSPHIDES

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The optical, electrical and photoelectronic properties of rare earth monophosphides (LnP, Ln=La, Nd, Sm and Y) have been studied. The experimental results indicate that their resistivities are low, the electric conduction in all of them is N-type, the energy gaps of LaP, NdP, SmP and YP are 1.46eV, 1.15eV, 1.1eV and 1.0eV, respectively. The SmP/Si and YP/Si junctions exhibit the photovoltaic effect. They may be used as photoelectronic sensors.

1. Introduction

Since the $III_A - V_A$ compound semiconductors, e.g. GaAs, GaP etc, have been widely used in modern photoelectronic devices, the compounds of rare earth and the V_A group elements are of interesting to study. Considerable research has been performed on the rare earth nitrides and arsenides, but less research about rare earth phosphides is available. Some works[1-4] reported the preparation and structure of rare earth phosphides. Hiscocks [5] and Yim [6] measured the resistvity and absorption spectra of SmP and ScP. The energy gap of SmP is 1.09eV, that of ScP is 1.1eV. Guntherodt and Kaldis [7-9] measured the resistivity of GdP and its reflection spectrum. They noted that GdP exhibits a metallic resistivity. Research about the other properties of LnP has not been found in the literature.

In order to explore the possibility of rare earth phosphides for applications, we have measured the optical, electrical and photoelectronic properties of several rare earth monophosphides.

2. Experimental

The LnP samples were prepared through mixing La, Nd, Sm, Y and phosphorus of 99.9% purity in stoichiometric proportion and evacuating, sealing in quartz ampules under 6.6×10^{-3}Pa, heating at 1100°C for 20 hour. The powder was then reground, pressed into pellets, and the pellets were evacuated and sealed in the ampoule again under 6.6×10^{-3} Pa, and then sintered at 1100°C for 10 hour.

The structure analysis was performed on Rigaku denki " 2028 D/max - II " X-ray powder diffractometer. The resistivity was measured with four-probe and Van de Pauw methods at room temperature. LnP films were deposited on optical glass and polished p-Si substrate under 6.6×10^{-3} Pa in GD-450B vacuum coating machine. The absorption spectra were measured with a Zeiss, VSU_2 -p spectrophotometer in the wavelength region of 300 to 2100 nm. The measurement of spectral response was made with a Zeiss, VSU_1 spectrophotometer.

3. Results and Discussion

3.1 Optical properties of LnP

The absorption spectra of LnP are given in Fig.1. No sharp absorption peaks produced by transitions of the 4f electrons appear. This suggests that the absorption only involves transitions of electrons between the conduction band and the valence band. The conduction band of LnP is formed by the 5d6s states of rare earths and the valence band is formed by the 3p

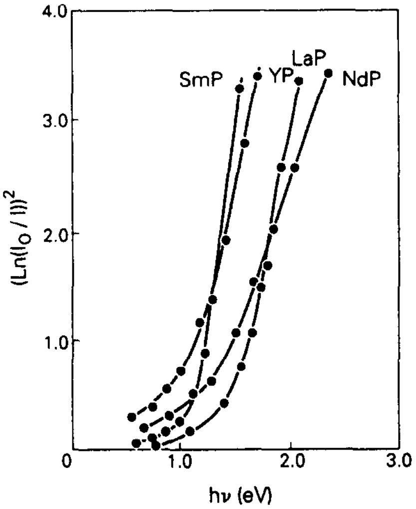

Fig.1 The absorption spectra of LnP

state of phosphorus.[7] Therefore, the absorption spectra are similar to these of direct transition semiconductors.

According to the current theory of photon absorption in solids,[10] an extrapolation of the linear portions of these absorption curves to $(\ln(I_0/I))^2 = 0$ was used as a measure of optical energy gaps. ($\ln(I_0/I)$) is the optical density) Thus, the Eg of LnP can be obtained from the absorption curves. The results are given in table 1.

It is also shown in table 1 that the Eg of SmP is 1.1eV. Our experimental result agrees with ref.5 but the energy gaps of the other LnP have not been found in literature.

3.2 Electrical properties of LnP

The measured electrical properties of LnP are also given in table 1. These results indicate that the resistivities of LnP are low, their carrier concentrations are high, with 10^{17} - 10^{19} cm^{-3}, the electric conduction in all of them is N-type. The low resistivity of LnP may be caused by the higher carrier concentrations.

The relationship between the resistance and temperature has been measured between 77 and 300K. It is evident that the resistance of LnP decrease fast with increasing temperature. LnP exhibits semiconducting behavior with negative temperature coefficient of resistance.

According to the equation,

$$R = A\exp(\Delta E/2KT)$$

Table 1 The properties of LnP

Compounds	LaP	NdP	SmP	YP
Lattice parameters(nm)	0.6025	0.5826	0.5760	0.5652
Energy gaps (eV)	1.46	1.15	1.1	1.0
Resistivities (-cm)	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)	-14.8		-1.94	-11.4
Carrier concentration n (cm^{-3})	4.2×10^{17}		3.2×10^{18}	5.5×10^{17}
Activation energy Eg (eV)	1.4×10^{-1} 283-353K	6.3×10^{-3} 93-233K	3.6×10^{-3} 85-193K 1.2×10^{-2} 193-228K	1.8×10^{-2} 116-148K 1.1×10^{-2} 163-308K

the activation energy can be calculated from the dependence of resistance and temperature. The results are given in table 1. It is shown that the activation energy is very small. This suggests that the Fermi level of LnP is very close to the conduction band. This may be the reason for the low resistivities in LnP. The optical and electrical properties show that LnP is N-type semiconductor.

3.3 Photoelectronic properties of LnP

In order to measure the photoelectronic property of LnP, the material was deposited on a polished p-Si substrate. The current-voltage characteristic of LnP/Si was measured and the results are given in Figs.2-3.

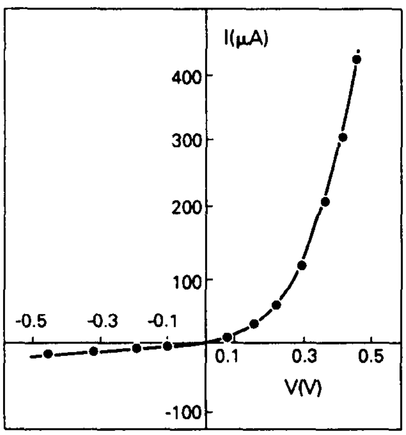

Fig.2 The dark I-V characteristic of SmP/Si junction

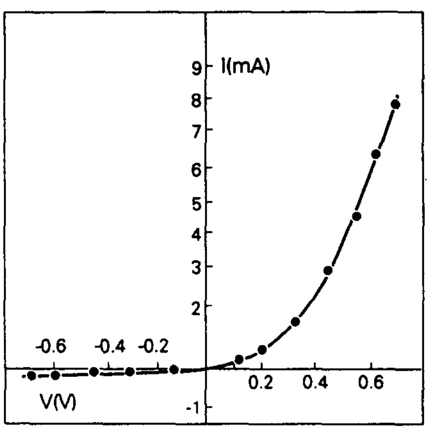

Fig.3 The dark I-V characteristic of YP/Si junction

It is shown in these figures that the forward current is very different from the backward current. When the positive voltage of 0.48V is applied across the SmP/Si the forward current is 0.52mA. However, upon application of a negative voltage of 0.44V the backward current is only 0.02mA. On the other hand, when the electric voltage of 0.74V is positively biased with respect to the YP/Si the forward current of 9.9 mA is obtained. When the electric voltage of 0.72 V is negatively biased the saturation current is only 0.41 mA. The marked rectifying characteristic of a p-n junction is displayed by the LnP/Si. It proves that a p-n junction is formed on the SmP/Si and YP/Si.

The spectral sensitivity of the LnP/Si junctions has been measured and the results are displayed in Fig.4.

The YP/Si junction exhibits photovoltaic sensitivity from 700 nm to 1200 nm, while a spectral response maximum at about 930 nm. The SmP/Si junction is spectral sensitive from 800 nm to 1200 nm, and its maximum lies about 985 nm. Comparing it with the results of Si and GaAs photovoltaic cells, the spectral sensitivity is from 360 nm to 1060 nm for the Si cell and 490 nm to 880 nm for the GaAs cell. The spectral sensitive region of the LnP/Si junctions shifts to the infra-red, compared with the visible.

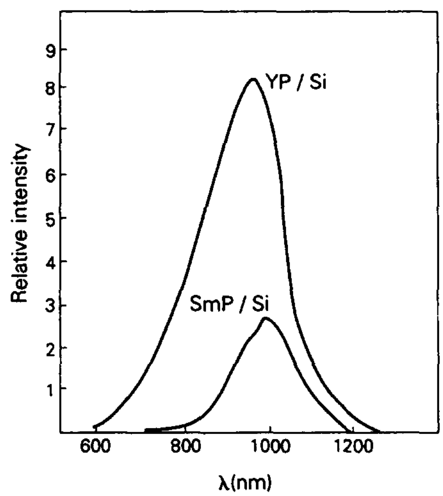

Fig.4 The spectral response curves of SmP/Si and YP/Si

For investigating the photovoltaic effect, the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) were measured under 100 mW/cm^2 illumination of a tungsten lamp. The results are given in table 2.

The value of J_{sc} and V_{oc} of p-Si is very small, and the YP/Si junction exhibits the largest J_{sc} and V_{oc} .

These behaviors make LnP may be applied in photolectronic sensors.

Table 2 the photoelectric properties of LnP/Si

	J_{sc} (mA/cm^2)	V_{oc} (V)
p-Si	8.5×10^{-3}	0.01
SmP/Si	4.10	0.15
YP/Si	16.8	0.30

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