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Application of Black Phosphorus to Infrared Detector

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The electrical and optical properties, especially photoconductive one, of an elemental black phosphorus semiconductor have been investigated. It has been found that the black phosphorus crystals show the photoconductive properties with a linear response for light intensity, a fast response less than about 1 μs and a selective response for polarized light. These results indicate that black phosphorus is applicable to IR detecting devices.

1. INTRODUCTION

The interesting solid state properties of black phosphorus (black P) have been considerably acknowledged.[1] The band gap of this elemental semiconductor is approximately 0.3 eV; so it may be used for infrared (IR) detection over a range of wavelength shorter than about 4 μm. This wavelength is of great practical importance for the realization of IR detecting devices, because a window in atmospheric transmission is observed in the 3-5 μm range. A mixed compound semiconductor $Hg_{1-x}Cd_xTe$ is a most suitable detector in this spectral range.[2] It is well known that the electro-optical characteristcs of devices critically depend on the semiconductor surface properties.[3,4] However, the surface properties of $Hg_{1-x}Cd_xTe$ have only to a limited extent been reported in the literature.[5-7] In addition, it is very difficult to the good single crystal with controlled composition because of the high Hg partial pressure and the Hg/Cd segregation.

In the present paper, we report a study of the electrical and optical properties, especially photoconductive one, of the elemental black-P semiconductor. These suggest that the black P can be used as an IR detecting device.

2. EXPERIMENTAL

Black P single crystals were grown from the solution of white P in liquid Bi. In the bismuth-flux method, red P can not be used directly, since red P does not dissolve in liquid Bi. On the other hand, white P of high purity is not available because of its chemical activity. Therefore, commercial white P must be purified by water-steam distillation. In the present study, we obtained high-purity white P from high-purity red P, using the method of conversion from red to white.[8] Since white P is quite poisonous , highly reactive and inflammable in air, it is undesirable to expose it to the air. Thus we devised a new bismuth-flux method in which both the conversion of red to white and

the crystallization of black P can be performed in an evacuated quartz-glass apparatus without breaking the vacuum. The details were described in the literature.[9] The needle-shaped crystals were about 5 mm in length and 10 to 100 μm in thickness. The film-shaped or plate-shaped crsytals were typically 1 to 10 μm in thickness and above 100 μm in width.

Optical absorption of a film-shaped black P crystal of 1.6-μm thickness was measured for light linearly polarized by the Glan-Thomson prism. Electrical conductivity was measured by the four-probe method, in which gold paste was used to make the electrical contacts between a small black P sample and Au wires of 50-μm diameter. Photocurrent of the black P sample was also measured in the same manner. The illuminated area of black P was only about 2×0.1 mm^2. The time respons of the photocurrent was measured under the excitation of a laser diode with 890-nm emission and 80-ns pulse width (Hamamatsu Photonics C2629).

3. EXPERIMENTAL RESULTS AND DISCUSSION

Black P has an orthorhombic layered structure and consists of double puckered layers parallel to the a-c plane. Figure 1(a) shows a single puckered layer of black P and its crystallographic axes. Figure 1(b) shows a schematic drawing of a plate-shaped black-P crystal. A needle axis corresponds to the a-axis. Electrical conductivity is high for the c-axis and low for the b-axis.[10,11] Figure 2 shows the optical absorption spectra of a film-shaped black-P sample for light linearly polarized in the a- and c-axes at liquid nitrogen temperature. The difference in the absorption below about 2.6 eV can be explained by the band structure of black P; that is, the absorption by the light polarized in the a-axis is due to forbidden transition, while the absorption in the c-axis is due to allowed one.[12,13]

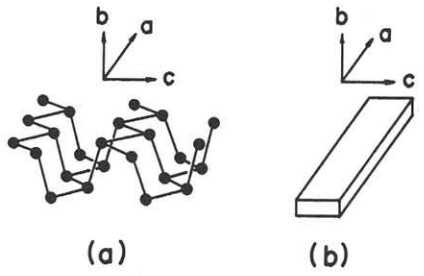

Fig.1 (a)A single puckered layer of black-P and its crystallographic axes. (b)A schematic drawing of a typical black-P plate-shaped crystal.

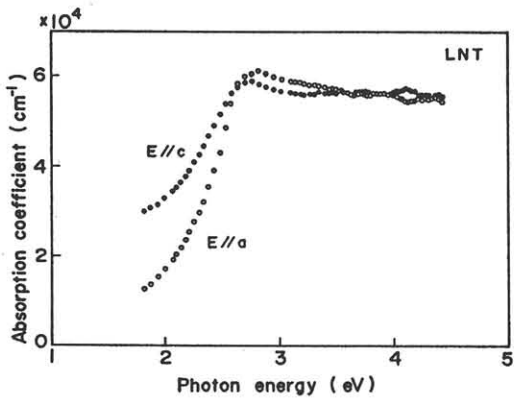

Fig.2 Optical absorption spectra of film-shaped black-P in the range from visible to near-infrared.

Figure 3 shows an electrical conductivity along the a-axis direction of a needle-shaped black-P sample in the dark. It indicates a typical temperature dependence of the impurity semiconductor. The band-gap energy was estimated to be 0.28 eV from the slope of intrinsic region.[9] Hall measurements show that the black P is a p-type semiconductor. It has a resistivity of ∿0.8 Ωcm, carrier concentration of ∿1×10^{16} cm^{-3}, and mobility of ∿500 cm^2/Vs at room temperature. The details of the transport properties of black P will be described elsewhere.

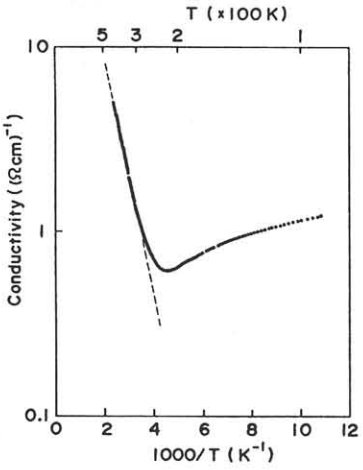

Fig.3 Temperature dependence of the a-axis conductivity of black P.

Figure 4 shows the a-axis photocurrent for the illumination of linearly polarized 1250-nm light as a function of angle between the c-axis and the direction of the polarization. The photocurrent for the light polarized in the a-axis is larger than for the light polarized in the c-axis. This result can be explained by the difference of the absorption spectra between the two directions of polarization (Fig.2). The angular dependence of hotocurrent enable us to detect the direction of polarization of IR light.

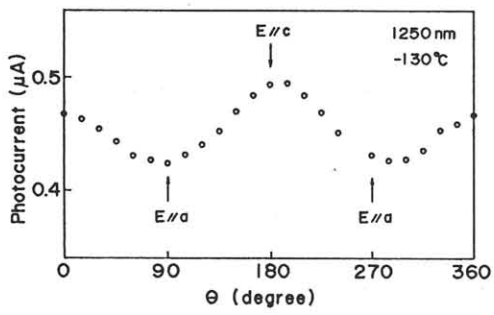

Fig.4 Angular dependence of the photocurrent of black P for linearly polarized 1250-nm light.

Figure 5 shows the spectral response of the photocurrent at several temperatures. The photocurrent rises up at 500 nm and increases with the wavelength. The maximum photocurrent is obtained at 1250 nm. Afterword, the photocurrent decreases with increasing wavelength. The drop of photocurrent in the short wavelength region may be due to the carrier recombination at the surface of black P because of large absorption coefficient. The fall of photocurrent in the long wavelength region results from the decrease in the dispersion efficiency of the prism monochromator (Hitachi EPU-2A). We have obtained the gradual increase of the photoresponse towards the 2-μm wavelength by calibrating it with the spectral response of the PbS detector (Hamamatsu P397).

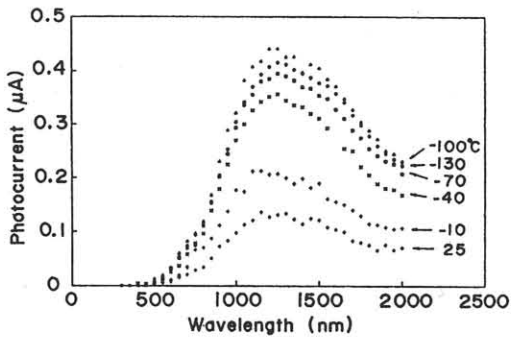

Fig.5 Spectral response of the photocurrent of black P for light polarized in the c-axis at several temperatures. Intensity of the incident light was not calibtated.

Figure 6 shows the temperature dependence of the photocurrent in the range from -130 C to room temperature. As the temperature increases, the photoresponse curve decreases gradually, showing a plateau arround -60 C. At room temperatur, a considerable photoresponse is still observable, this making us an expectation that the black-P photodetector operates at room temperature. The plateau may be concerned with the minimum conductivity in this temperature region as shown in Fig.3.

Figure 7 shows a linear relation between the photocurrents of the black-P sample and the PbS detector. The light

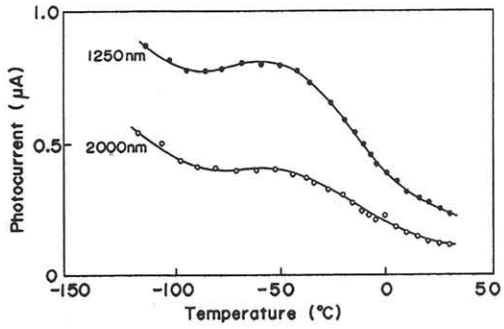

Fig.6 Temperature dependence of the photocurrent of black P for 1250- and 2000-nm lights polarized in the c-axis.

intensity of the 1250-nm light was changed at room temperature. The linearity between the photocurrents of two different detectors indicates that the photocurrent of black P is in proportion to the light intensity, since it is known that the PbS detector has a linear response for light intensity.

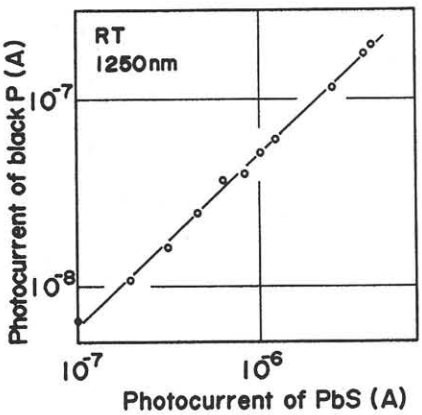

Fig.7 A linear relation between the photocurrents of black P and PbS for the illumination of 1250-nm light at room temperature.

The time response of the black P photodetector was investigated as follows. A constant voltage of 9 V was applied in series to the black P and a standard resistor of 1 kΩ . When the black P was illuminated with a light pulse (890nm, 80 ns) from the laser diode, a transient voltage generated across the resistor was displayed on an osilloscope (Toshiba 10065). The time response of the black P was roughly estimated to be less than 1 μs from the decay curve of the voltage which contained a considerable noise.

In conclusion, the black-P crystal shows the photoconductive properties with a linear response for light intensity and a selective response for polarized light in the near IR region. The response time is less than 1 μs which is comparable with those of other photoconducting cells. Fabrication of black-P p-n junction or Shottky contact and the investigation of its photovoltaic effect are also important for further application of black P.

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