March, 1991] Bull. Chem. Soc. Jpn., 64, 811—813 (1991)

Electrical Conductivity of Black Phosphorus-Germanium Compound

Yusei MARUYAMA,* Tamotsu INABE, Lin HE, Toshifumi TERUI,† and Kokichi OSHIMA††
Institute for Molecular Science, Myodaiji, Okazaki 444
† Graduate University for Advanced Studies, Myodaiji, Okazaki 444
†† Department of Physics, Okayama University, Tsushimanaka, Okayama 700
(Received October 4, 1990)

Single crystals of a new material, black phosphorus doped with germanium, have been prepared by a bismuth-flux method. Germanium atoms are incorporated into the black phosphorus in 2 to 4 atomic percent. The resistivity is reduced by two to three orders ($\rho=6\times10^{-3}\ \Omega$ cm) compared with the pure black phosphorus, and its temperature dependence is metallic at low temperatures. There is no magnetoresistance up to 12 T at 0.6 K in striking contrast to the pure black phosphorus which shows negative magnetoresistance in this region. The crystal lattice constants decrease with germanium doping, especially in the interlayer direction. These facts indicate the enhanced three dimensionality with germanium doping.

Black phosphorus discovered by Bridgman in 1914[1)] has been known to be a layered structure narrow gap semiconductor[2)] and to have interesting properties, such as pressure-induced structural phase transitions,[3)] anomalous superconductivity,[4)] and two-dimensional Anderson localization.[5)] A chemical modification of black phosphorus is a potentially promising strategy to realize a metallic phase in black phosphorus under normal pressure.

As the first approach to prepare new chemical species based on black phosphorus we have tried to synthesize black phosphorus intercalation compounds with cesium[6)] and iodine.[7)] The second trial was a doping of silicon, a IV group element, to increase the positive hole character in black phosphorus (a V group element). The doping of silicon realized a somewhat metallic character in black phoshporus.[8)]

In this report we describe the effect of germanium doping into black phosphorus. Almost metallic temperature dependence was observed for the electrical resistivity at low temperatures, and no magnetoresistance was found out. Substantial decrease in the lattice constants was recognized with germanium doping, especially in the interlayer direction.

Experimental

Doping of germanium was carried out by mixing it into melted bismuth with black phosphorus powder. By very slow cooling of the melt very tiny crystals were obtained (typical size: $500\times15\times3\ \mu m^3$). The incorporated amount of germanium was detected by an Electron-Probe-Micro-Analysis technique (EPMA).

Electrical resistivity and its temperature dependence were measured with a four-probe method from 300 to 0.6 K in the ^{3}He cryostat system. Magnetoresistance was also examined by the use of a superconducting magnet up to 12 T at low temperatures. The change in lattice constants caused by the incorporation of germanium was detected by an X-ray diffraction analysis.

Results and Discussion

The resistivity of a germanium doped single crystal at room temperature is lower by almost three orders compared with a pure black phosphorus: $\rho(RT)=6\times10^{-3}\ \Omega$cm. The relative amount of germanium which is incorporated in black phosphorus was roughly estimated to be 2 to 4 atomic percent from the result of EPMA. The corresponding amount of silicon which was included in black phosphorus-silicon was about 0.01 atomic percent.[8)] Germanium is far better introduced into black phosphorus compared with silicon in spite of larger covalent radius of the former, and this causes the remarkable reduction in the resistivity.

The lattice constants of a single crystal of germanium doped black phosphorus, PGe_x ($x=0.03\pm0.01$), were found by an X-ray diffraction analysis and

Table 1. Comparison of the Lattice Constants of PGe_x ($x=0.03\pm0.01$) and Those of Black P

	a/Å	b/Å	c/Å
Black P[9)]	3.3136	10.478	4.3763
PGe_x	3.310	10.42	4.364
Difference	−0.004	−0.058	−0.012
		(0.6%)	(0.3%)

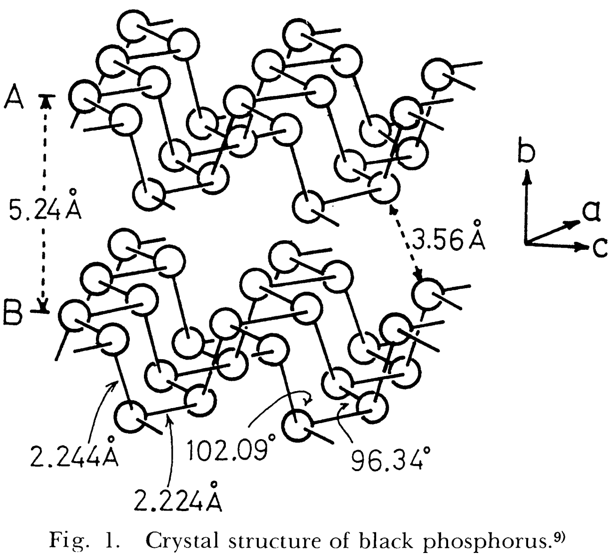

Fig. 1. Crystal structure of black phosphorus.[9)]

they are shown in Table 1 together with those of black phosphorus.[9] All lattice constants become shorter, especially in the b-axis, interlayer direction (Fig. 1), substantially shorter. In the c-axis direction, the rate of reduction is almost the same order as in the b-axis direction, and in the a-axis direction there is almost no reduction within the experimental error. This fact is just corresponding to the pressure dependence of the

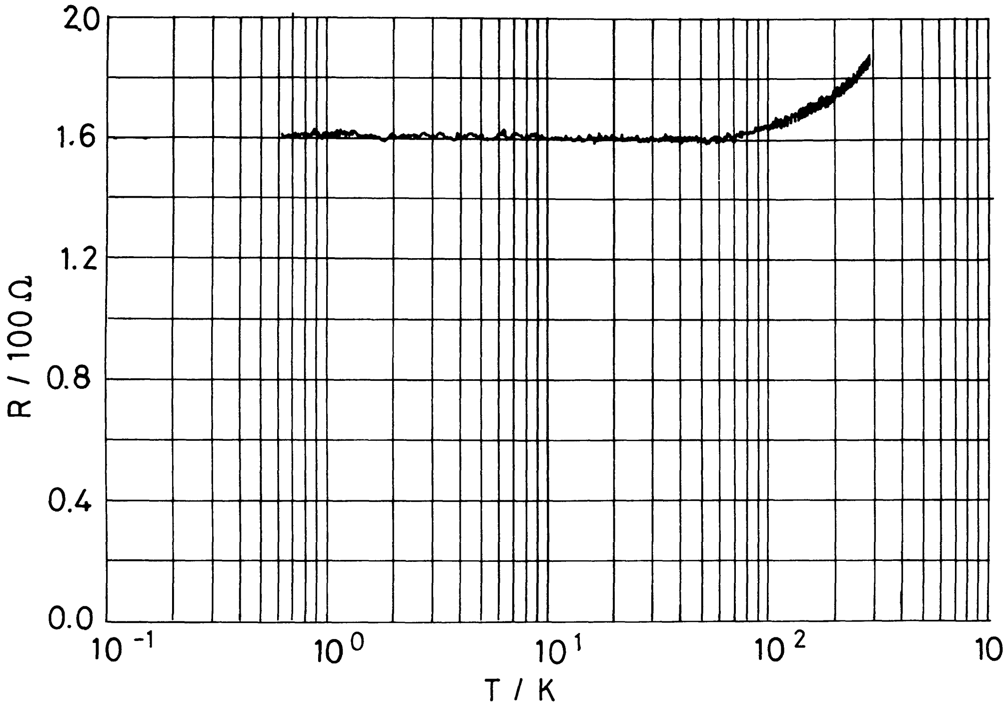

Fig. 2. Temperature dependence of the resistance of PGe$_x$ (x=0.03±0.01).

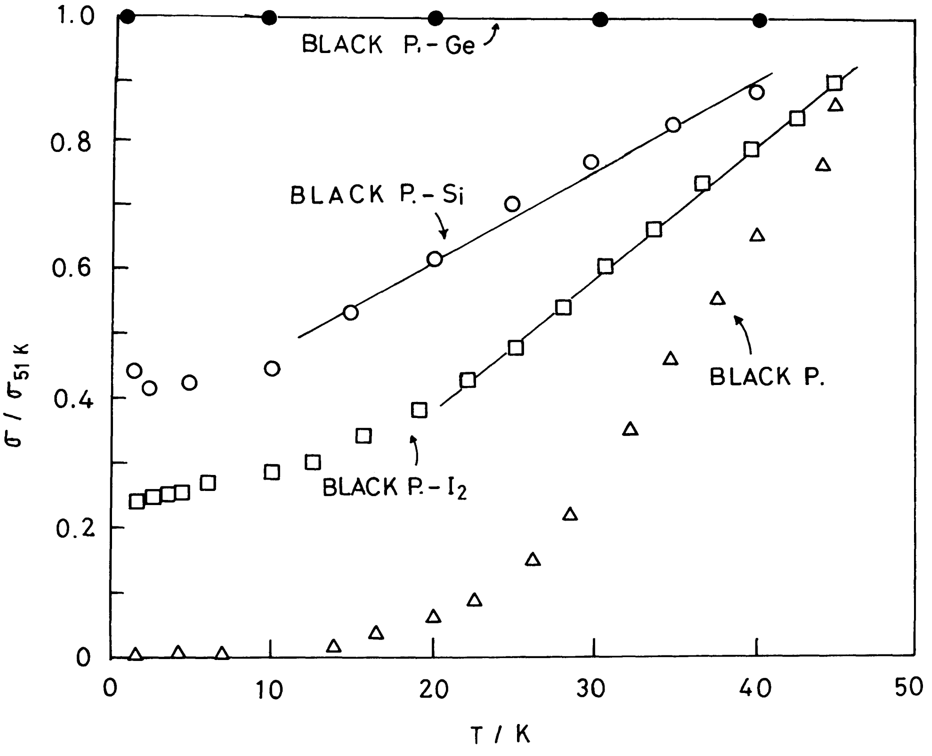

Fig. 3. Temperature dependence of the normalized conductivities ($\sigma(T)/\sigma(51\ K)$) of black phosphorus, black phosphorus-I_2, black phosphorus-Si, and black phosphorus-Ge.

lattice constants of black phosphorus.[10] In pure black phosphorus, the semiconducting gap energy is strongly dependent on the interlayer interaction, and thus the reduction in the b-axis length of PGe_x may lead reasonably to lower resistivity.

The temperature dependence of the resistances of PGe_x ($x=0.03\pm0.01$) is shown in Fig. 2. It shows almost metallic behavior from 300 to 0.6 K, and below 50 K the resistance is almost constant. This behavior clearly contrasts with the case of pure black phosphorus in which the resistivity has an exponential rise at low temperatures. Even in PSi_x there is small rise in the resistivity at low temperatures. Figure 3 shows the different behaviors of the conductivity ratios ($\sigma(T)/\sigma(51\ K)$) below 50 K in pure black phosphorus and its intercalated or doped compounds.

The magnetoresistance of PGe_x was investigated at 0.6 K up to 12 T applying the magnetic field along the b-axis with the electric current along the a-axis since black phosphorus is known to have negative magnetoresistance at low temperatures.[2,5] There is, however, no indication of magnetoresistance in PGe_x at all in this range of magnetic field at 0.6 K.

These two findings, metallic behavior and no magnetoresistance, may be partly ascribed to the enhancement of three dimensional character due to the reduction in the interlayer distance with the doping of germanium. It was reported that the semiconducting energy gap of black phosphorus is dependent on pressure and it vanishes over 1.8 GPa.[11] The reduction of the lattice constants around 2.0 GPa is about 2.5% in b or c-axis. The differences in the corresponding lattice constants are about 0.3—0.6% in Table 1. The reduction of the lattice constants is not large enough for vanishing the semiconducting gap of black phosphorus, but the enhanced number of holes in the filled band may be responsible for the appearance of metallic nature in PGe_x.

In conclusion, we have succeeded in the synthesis of germanium doped black phosphorus, and determined the composition, $PGe_{0.03\pm0.01}$, and the lattice constants of the new compound. The metallic behavior was observed by the temperature dependence of the resistivity at low temperatures, and such behavior is reasonably explained by referring to the change in the lattice constants on doping.

References

1) P. W. Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914).

2) Y. Maruyama, S. Suzuki, K. Kobayashi, and S. Tanuma, *Physica B*, **105**, 99 (1981).

3) S. Narita, S. Terada, S. Muro, Y. Akahama, and S. Endo, *J. Phys. Soc. Jpn.*, **52**, 3544 (1983).

4) H. Kawamura, I. Shirotani, and K. Tachikawa, *Solid State Commun.*, **49**, 879 (1984).

5) N. Iwasaki, Y. Maruyama, S. Kurihara, I. Shirotani, and M. Kinoshita, *Chem. Lett.*, **1985**, 119.

6) Y. Maruyama, S. Suzuki, T. Osaki, H. Yamaguchi, S. Sakai, K. Nagasato, and I. Shirotani, *Bull. Chem. Soc. Jpn.*, **59**, 1067 (1986).

7) T. Nishii, Y. Maruyama, T. Inabe, and I. Shirotani, *Synth. Met.*, **18**, 559 (1987).

8) Y. Maruyama, T. Inabe, T. Nishii, L. He, A. J. Dann, and I. Shirotani, *Synth. Met.*, **29**, F213 (1989).

9) A. Brown and S. Rundqvist, *Acta Cryst.*, **19**, 684 (1965).

10) L. Cartz, S. R. Srimivasa, R. J. Riednev, J. D. Jorgensen, and T. G. Worlton, *J. Chem. Phys.*, **71**, 1718 (1979).

11) Y. Akahama, S. Endo, and S. Narita, *J. Phys. Soc. Jpn.*, **52**, 2148 (1983).