COMBINE TECHNIQUE OF CONDUCTING MATERIALS TESTING AT HIGH PRESSURES

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ABSTRACT

The technique of investigations of resistance $\rho$, thermoelectric power $S$, and galvanomagnetic properties of materials by the two-terminal method of measurements under pressure up to 30 GPa is discussed. The combine of stationary and non-stationary regimes of treatment, variation of high pressure chambers with conducting or insulating plungers and using of simultaneous and parallel measurements of various properties are proposed to estimate the parameters of materials under testing. The results of investigations of initial semiconductor and high pressure metal phases of Ge, Te, and molecular solid -Iodine up to 30 GPa at the diamond-plungers apparatus are represented. The technique may be useful for semiconductor fabricated device treatment.

Keywords: pressure, phase transition, inclusion configuration, magnetoresistance, Hall effect, thermoelectricity, diamond electrodes

Electrical, thermal and magnetic properties of semiconductor materials and fabricated devices are a complex functions of electron structure parameters and of the form and concentration of various components. For homogeneous semiconductor with several type of charge carriers a conductivity $\sigma = 1/\rho$ shows total positive contribution of all electron bands, independent on the sign of charge carriers, while thermoelectric power $S$ depends on the sign of charge carriers and partial conductivity of bands $\sigma_i$:

$$\sigma = \sum \sigma_i = \sum n_i \mu_i$$

$$S = \sum S_i \sigma_i / \sigma,$$

where $\mu_i$ and $n_i$ are the mobilities and electron (holes) concentrations of individual bands. Hall constant $R$ and transverse magnetoresistance $\rho$ in magnetic field $B$ in case a several bands give the contributions are:

$$R = \langle R\sigma^2 \rangle \left/ \left(\langle \sigma \rangle^2 + \langle R\sigma^2 \rangle B^2 \right) \right.$$  

$$\rho = \langle \sigma \rangle \left/ \left(\langle \sigma \rangle^2 + \langle R\sigma^2 \rangle B^2 \right) \right.$$

where the entities in the angle brackets are equal

$$\langle \sigma \rangle = \sum_i \left[ \sigma_i / (1 + (R_i \sigma_i B^2)) \right], \quad \langle R\sigma^2 \rangle = \sum_i \left[ R_i \sigma_i^2 / (1 + (R_i \sigma_i B^2)) \right],$$

and $R_i$ and $\sigma_i$ are Hall constant and conductivity of individual $i$-electron bands.

The inhomogeneous mixture of uniform phases depends also on concentration and shape of phase inclusions. A substance may become inhomogeneous, for example, at the region of pressure-induced phase transition. The model of oriented inclusions was applied for such heterophase material; the configuration being variable from the case of parallel to a
consequent electrical connections of phases. The resistivity $\rho$ or conductivity $\sigma=1/\rho$ (and thermal conductivity $\lambda$) in this approach are viewed as a normalized sum of phase contributions in two equivalent considerations of "consequent" and "parallel" electrical (thermal) connection of phases.

$$\rho = \sum c_i \cdot \rho_i \cdot f_i \cdot \left( \sum c_i \cdot f_i \right)^{-1}, \quad \sigma = \sum c_i \cdot \sigma_i \cdot f_i(\sigma) \cdot \left( \sum c_i \cdot f_i(\sigma) \right)^{-1},$$

where sum of phase concentrations $c_i$ is equal to 1 and phase configuration parameters along the electrical current are $f_i=3\rho/[A\rho+(3-A)\rho_i]$ and $f_i(\sigma)=3\sigma_i/[A\sigma\sigma+(3-A)\sigma_i]$. For constant $A$ equal to 0, 3 and 1 the Eq. 5 coincides respectively with the cases of parallel and consequent electrical connections, and the spherical shape of phase inclusions. Hall constant and $S$ may be written in the similar additive forms

$$R = \left( \sum c_i \cdot R_i \cdot f^j_i \cdot f_i^H \right) \cdot \left( \sum c_i \cdot f^j_i \cdot f_i^H \right)^{-1},$$

where $R_i$ is a Hall constant of $i$-phase, determined by Eq. 1-4, and configuration parameters $f_i^j$ and $f_i^H$ correspond to the directions of electrical current and Hall voltage respectively.

To determine the parameters of electron bands the parallel measurements of several kinetic effects (1)-(4) have to be done. High pressure measurements due to electron bands shifts are known to be the crucial instrument for unambiguous estimation of the set of the above parameters of materials. Analogous test of the electron parameters of different phases at inhomogeneous materials request the complex investigation at high pressure $P$ of the above properties, and additionally the concentration $c_i$ and configuration of phases have to be taken into account.

In present paper the technique of investigations of the above properties of materials under pressure is discussed.

**EXPERIMENTAL TECHNIQUE**

For samples compression we've using the high pressure chambers of "piston-cylinder" type with one- or two-layers body for hydrostatic pressure generation up to 1.2 and 2.3 GPa respectively (Fig. 1) and solid media apparatuses with the plungers made of various hard materials up to 30 GPa (Fig. 2, 3). The most parts of chamber were made from non-magnetic titanium alloys. For galvano-magnetic measurements the autonomous versions of these high pressure chambers are used.

Hydrostatic pressure-transmitting media were mixtures of transformer oil and kerosene (Fig. 1), and the pressure gauge were resistance sensors. The inner diameter of chamber was 4 mm., and typical sizes of samples were $-5 \times 0.7 \times 0.7$ mm$^3$. After the pressure generation the position of plungers was fixed by female screw for magnetic field and low temperature measurements. Due to two-layers construction the chambers allow safe exploring under pressure fixed in a several months.

Fig. 1. Two-layers hydrostatic pressure "piston-cylinder" chamber, 1- body, 2,3- plungers, 4 - female screw , 5 - liquid medium, 6 - pressure gauge , 7 - a sample , 8 - electrical leads from a sample, thermocouples and $P$-gauge.

Solid media high pressure device for pressure generation up to 30 GPa with variable plungers includes the pressure apparatuses (Fig. 2) and recording block. The recording block contains the microprocessor, interfaces for the connection of the outputs of standard digital voltmeters, communicated with the sensors of plunger displacement, pressure (stress), temperature, and electrical voltage of sample. For the thermoEMF $S$ -measurements under pressure the heater and
temperature control sensors were set at the plungers (Fig. 2). The synthetic diamonds plungers of the device serve as thermal and voltage probes to a sample up to 30 GPa \(^{8,9,21,23,29}\). The temperature controller was used for operation by the heaters work in the pressure chamber and for producing of the stationary and non-stationary thermal regimes during the testing. The experimental data are stored in the energy supply independent RAM, and may be read out from the display or transferred to IBM-PC by serial interface \(^{8,21,23}\). The removable cassette 6 with various type pressure plungers and container with a sample between them simplified the quick change of samples during investigations.

High pressure plungers of Bridgman anvils type \(^{19,20,30}\) made of steel, tungsten carbide and superhard materials were used for pressure generation up to 5 GPa (Fig. 3a), 10 GPa (Fig. 3b, c) and 30 GPa (Fig. 3d), respectively. We used different versions of plungers by variation of superhard materials and the construction of plungers to enlarge the pressure range. The good results were received for the two-layers plungers consisting of sintered diamond tips and tungsten carbide matrices, produced at high pressures and temperatures \(^{21-23}\). The values of \(P\) are estimated from the acting stress \(F\) and tabulated dependencies \(P(F)\), recording for the any pair of pressure plungers \(^{21,26,30,31}\).

The boron nitride and the synthetic diamond without metal impurities we've used as a tip of plungers have a high electrical resistivity, so the platinum-silver ribbons of ~ 5 \(\mu\)m thick are used to get electrical outputs to a sample. The other synthetic diamonds used are high conducting materials due to metal inclusions and so are good as an electrical probes to a sample for the electrical measurements \(^{21-24,26,27}\). The usual sizes of high pressure area for a samples were ~ 0.2-0.5 mm in diameter and ~ 0.1 mm - in height. The fine samples of 10-20 \(\mu\)m thickness were tested in the device. The pressure transmitting medium was a lithographic stone \(^{8,19,30}\). The various pressure distribution near the samples for the different kind of pressure plungers (Fig. 1-3) and also the variation of plungers materials provide the better accuracy of combine measurements.

For hydrostatic treatment of samples at \(P > 2\) GPa the modern diamond-anvils (and sapphire anvils) apparatuses where the truthful hydrostatic pressures are generated \(^{30-34}\) were used (Fig. 4). Pressure was determined with an estimated error ~2 kbar from the shift of the R1 fluorescence line of ruby, exited by helium-cadmium laser \(^{30-33}\). A small chip of ruby (~20 \(\mu\)m) was also placed near the sample in liquid pressure-transmitting medium. Since the longest size of the sample set in diamond (or sapphire) anvil cell is ~100 \(\mu\)m, a special optical apparatus is needed to observe the sample surface and to measure reflection spectra from such a micro-sample. The light from a tungsten halogen lamp was collected with a fused

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Fig. 2. High pressure apparatus. 1— table, 2 — lever mechanism, 3 — pressure chamber, 4 — sensor of plunger displacement, 5 — reduction gear with the electromotor and handle drives, 6 — removable cassette with pressure anvils, container and a sample, 7 — thermal regulators, 8 — sensor of plunger stress, 9 — sensors of lever springs contraction.

Fig. 3. Various versions of high pressure plungers and appropriate shape of container for a sample: a) "cupped" anvils; b), c) toroidal high pressure cells: b) cupped central part; c) flat central part; d) superhard anvils \(^{30,31,19,20}\). The plungers of a) kind were made usually of steel, b) and c) - of tungsten carbide, and d) - of sintered diamonds or boron nitride. Above and below the container there are the upper ad lower pressure plungers; dark area show the volume for a sample placement.

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lens and focused on the aperture of a pinhole. The image of this aperture was focused onto sample in the cell by a spherical mirror and a beam splitter. The reflected light from the sample was collected with a fused lens, and focused on a second pinhole. The recording of ruby luminescence and the reflected light from a sample was performed by spectrometer (Fig. 4).

By using of this apparatus the observations of phase transformation from zinc blende to cinnabar structure at HgTeS, HgSeS single crystals were performed, and the traces of plastic deformations connected with these reversible transitions were observed, while the resistivity, volume and thermoelectric power changes during this transformation were detected by all the chambers shown at Fig. 1-3.

The apparatuses described were using for the proposed combined investigations of the semiconductors undergoing pressure-induced phase transformations. The combine of stationary and non-stationary regimes of treatment, variation of high pressure chambers with conducting or insulating plungers and using of simultaneous and parallel measurements of various properties allow to estimate the parameters of materials under testing.

RESULTS

The data of stationary and non-stationary regimes of treatment under pressure as in the previous and in this work were in good agreement with the results of investigations by current techniques. The pressure-induced phase transitions were investigated by simultaneous testing of various properties of materials by using of pressure devices shown at Fig. 1-4. For example, resistivity of Ge suffer a drop at phase transition into tetragonal metal phase near \( P = 9 \) GPa.

Fig. 5. The dependence of thermoEMF \( S \) on pressure for \( p \)-Ge single crystal at \( T = 295 \) K received by using of synthetic diamond apparatus. The electrical outputs to a sample were platinum-silver ribbons (triangles, solid line) and diamond conducting anvils (circles, dashed line).

ThermoEMF of Ge suffer a drop at pressure-induced phase transition into tetragonal \( \beta \)-Sn structure near \( P = 9 \) GPa (Fig. 6).

Fig. 6. Dependence of temperature difference between tungsten carbide (open symbols, two samples) and synthetic diamond anvils (solid symbols) obtained for \( p \)-Ge under the regime of constant density of thermal flux. The arrow shows the pressure of structural phase transition. Dependences of \( \Delta T(P) \) were obtained simultaneously with the recording of \( S(P) \) data.
5). The value of thermoEMF for high pressure phase may be estimated by the relative variation in respect with initial known value. The increase of the hole conductivity during this semiconductor-metal phase transition \( \rho \) tends to rising of thermal conductivity. So, the temperature gradient between different type pressure anvils fell at this \( P \) at constant density of thermal flux (Fig. 6), as well, as at non-stationary thermal flux. It’s interesting to point out, that the dependencies of \( \rho, S \) and \( \Delta T \) are disproportionate due to various values of these entities. The using of diamond anvils, or silver-platinum ribbons as an electrical outputs, allowed to put the correction to the results of \( S \)-measurements, and so to detail the value of \( S \) for high pressure phase.

For molecular solid Iodine increasing of conductivity due to gradual closing of forbidden energy gap in electron spectrum\(^{1,2,33} \) tends to enlarging of thermal conductivity \( \lambda \), so the thermal gradient \( \Delta T = \lambda / \lambda \) is falling (Fig. 7). Resistivity and \( S \) of Iodine is known to change during the structural transition at \( P = 21 \) GPa from molecular to monatomic phase. The behaviour of temperature gradient between the diamond plungers show that there is a peculiarity owing to the anomaly of thermal conductivity in the vicinity of this point at non-stationary and constant density of thermal flux (Fig. 7). Note, that anomaly of \( \rho \) and \( S \) are sufficiently smaller, than one of \( \Delta T \).

For single crystal Te by the above technique we observed the decreasing of \( S \) but \( MR \) rising under pressure applied up to \( 4 \) GPa due to closing of direct forbidden gap\(^{1,2,41} \). The results of \( MR \) measurements at diamond anvils (Fig. 8) coincide qualitatively with the hydrostatic \( P \) data up to \( 1.2 \) GPa\(^{41} \) and with those obtained with tungsten carbide anvils up to \( 7 \) GPa (the present work).

![Fig. 7. The dependence of temperature gradient \( \Delta T \) between the diamond anvils for Iodine sample on pressure. The peculiarity of \( \Delta T \) near \( P = 20 \) GPa corresponds to a phase transition point.](image)

Magnetoresistance of Te under pressure have near parabolic dependence on magnetic field \( B \) according to Eq. 3 for weak-field approximation\(^{3} \), and the mobility of holes was estimated from these curves. The increase of \( MR \) and holes mobility under pressure found for Te and Se below the Semiconductor-Metal (S-M) transition point\(^{24} \) is consistent with the vanishing of band gaps\(^{1,2,41,42} \). The inversion of \( MR \) sign from positive to negative was observed near \( P = 1.5-2 \) GPa, where the reconstruction of upper valence band of Te was predicted\(^{41,42} \) (fig. 8.b). The negative \( MR \) may be connected with the

![Figure 8 (a). Magnetoresistance of Te sample in diamond anvils at \( T = 300 \) K at fixed pressure \( P \), GPa: 1-10; 2-12; 3-13.7; 4-14.2.](image)

![Figure 8(b). Magnetoresistance of Te sample in diamond anvils at \( T = 77 \) K at fixed pressures \( P \), GPa: 1-0.6; 2-2.2; 3-3.2; 4-13.7; 5-14.2.](image)
magnetic field induced redistribution of holes between the closely lying valence band tops and the resulting mobility increasing \(^{24,41,42}\). This electron bands reconstruction under pressure doesn’t appear so clear in the rest kinetic effects\(^2\). Above the S-M transition (\(P>4\) GPa) as \(S\) and \(MR\) dropped, because of degeneration of hole gas \(^3\), but near the point of structural phase transition at 11 GPa \(^4\) the value of \(MR\) was rising (Fig. 8a), that supposed the appropriate rising of hole mobilities in new phase\(^2\).

The results of investigations of some other semiconductors - Si, Se, ternary chalcogenides of Ga, Bi, In, Hg, metals Cu, Au, ceramics YBaCuO, layers misfit crystals (PbS)TiS\(_2\) etc. up to 30 GPa by the above technique allowed to test the electrons and holes densities and mobilities at initial and high pressure phases \(^22-29,44\). We see, that the peculiarities of electron structure may be seen from various properties of substances during phase transitions. And the influence of inhomogeneous in the vicinity of phase transition point is different for various entities. So, the combine technique under consideration may be useful as for phase transition observations, and for semiconductor fabricated device treatment.

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