SELENIUM AS A POLYMERIC SEMICONDUCTOR AND THE MECHANISM OF ITS CONDUCTIVITY

PHYSICS

1966

SovietRxiv

Abstract

Full Text

UDC 621.315.592.2:546.23

PHYSICS

G. M. ALIEV, D. Sh. ABDINOV, S. I. MEKHTIEVA

SELENIUM AS A POLYMERIC SEMICONDUCTOR AND THE MECHANISM OF ITS CONDUCTIVITY

(Presented by Academician V. A. Kargin on July 23, 1965)

Selenium, owing to its physical properties, is a semiconductor whose applications in modern technology are highly diverse. This is apparently due to the fact that selenium, as an inorganic high polymer, possesses amorphous, α- and β-monocrystalline, hexagonal modifications, with ring-shaped, chain, and spiral molecules containing different numbers of atoms.

Although many works have been devoted to the study of the electrical properties of selenium, the mechanism of its conductivity remains unclear, and the experimental data obtained are contradictory. The effects of various impurities, especially oxygen, on the electrical properties of selenium have also been insufficiently studied, and the individual data refer to crystalline selenium ([1], [2]). The region of melting and the liquid state remains completely unexplored.

In order to clarify these questions, the present work gives a comprehensive study of the electrical conductivity (σ), thermoelectric power (α), and the Hall effect in solid and liquid selenium (from 20 to 450°), including the melting region.

The experiments were carried out on selenium of grade B_5 (99.99999%) before and after deoxygenation, as well as after various degrees of oxygenation and with oxygen-compensating impurities (Sb, Cd, Mn), which made it possible to determine the influence of oxygen on the physical properties of selenium. Deoxygenation was carried out according to ([2]), and the indicated parameters were measured by the methods ([3]–[5], [9]). The values given for the physical parameters are equilibrium values, since their time dependence was taken into account in the measurements ([2]).

Figure 1 shows the temperature dependence of σ (curve 1), the Hall coefficient R (curve 2), and the Hall mobility of the current carriers U (curve 3) of selenium. It is seen that σ of selenium in the solid and liquid states increases exponentially with temperature (with activation energies of 0.075 and 0.95 eV, respectively), decreasing discontinuously on melting. The exponential dependence of σ is entirely due to the exponential growth of the mobility of the current carriers,

Fig. 1. Temperature dependence of the electrical conductivity σ (1), Hall mobility U (2), Hall constant R (3), and calculated mobility (4) of current carriers in selenium

Figure 1: Fig. 1. Temperature dependence of the electrical conductivity σ (1), Hall mobility U (2), Hall constant R (3), and calculated mobility (4) of current carriers in selenium

since R in the solid and liquid states changes hardly at all with temperature (curve 2), which indicates the constancy of the concentration ($\sim 10^{15}$ cm^{-3}) of current carriers with changing temperature. The jump-like decrease of σ upon melting is caused both by a decrease in the concentration n (by $\sim$ 10 times) and by a decrease in mobility (by $\sim$ 80 times). The independence of the concentration of current carriers from temperature shows that crystalline and liquid selenium in the indicated temperature range is an impurity semiconductor and that all impurity centers are ionized.

In works (6-8), the small value of the mobility and its increase with temperature in crystalline selenium are explained by the fact that individual well-conducting crystallites are surrounded by high-resistance amorphous interlayers, which play the role of an energy barrier in the motion of carriers

current. However, such an assertion about the existence of "two phases" in selenium is not fully justified, since at present there are a number of works that refute this assertion (9,10). The increase of U with temperature in liquid selenium, where there are no crystallites, also contradicts the indicated interpretation. The mobility of current carriers in selenium crystallized under pressure is less than in selenium crystallized in the atmosphere (11); it increases with temperature also in amorphous selenium (12), which does not confirm the assumption cited.

In explaining the temperature dependence of U we proceed from the polymeric structure of selenium (13). The mechanism of conductivity of polymers consists of two processes: the motion of current carriers along the molecule and their jump transition from molecule to molecule (14). Since the frequency of these jumps is determined by the factor $e^{-\Delta E/kT}$, the U of current carriers increases with temperature according to the formula (15–17)

$$U = \frac{d^2\nu}{kT}\, e^{-\Delta E/kT}, \tag{1}$$

where $d = a\sqrt{2}/4$ (a is the lattice parameter), ν is the frequency of lattice vibrations, k is Boltzmann' s constant.

Fig. 1. Temperature dependence of the electrical conductivity σ (1), Hall mobility U (2), Hall constant R (3), and calculated mobility (4) of current carriers in selenium.

Fig. 2

Figure 2: Fig. 2

Taking $\Delta E \sim 0.075$ and 0.95 eV, respectively, in solid and liquid selenium, the temperature dependence of the mobility of current carriers was calculated from formula (1) (Fig. 1, curve 4). The calculated values of U agree well with the experimental data. The decrease of U upon melting is explained by an increase in the distance between the molecules (from 3.46 to 3.74 Å) of which crystalline and liquid selenium are built, since this leads to an increase in the intermolecular barriers, i.e., to an increase in ΔE.

According to ([18]), in selenium upon melting the short-range order and coordination number change only slightly. It follows from this that the concentration of current carriers upon melting of selenium should not change ([19,20]). Apparently, the decrease of n upon melting is associated with the weakening of the action of impurities in the liquid state, since active impurities in crystals are not active in the amorphous and liquid states ([20]).

Figure 2 presents the temperature dependence of σ of selenium before and after deoxidation (curves 1 and 2, respectively), and also after subsequent oxidation (curves 3-5). Oxidation of deoxidized selenium was carried out in an oxygen atmosphere at 215°C for 40, 150, and 350 hours.

As is seen from Fig. 2, after deoxidation σ at 20°C decreases by ~ 1000 times (relative to the initial value); from 20 to 150°C it slowly decreases with temperature, and after 150°C it increases with an activation energy of ~ 0.6 eV. The jump in σ upon melting of selenium after deoxidation almost disappears. Selenium before deoxidation has p-type conductivity in the solid and liquid states; after deoxidation it becomes electronic ([21]).

Curves 3-5 in Fig. 2 show that the change in σ caused by the action of oxygen is reversible. After heating deoxidized selenium in an oxygen atmosphere at 215°C for 350 hours (Fig. 2, curve 5), the value and temperature dependence of σ approach the initial ones. The change of α ([3,5]) upon deoxidation is also reversible.

Similar results, obtained upon deoxygenation, are also obtained when impurities of Sb, Cd, and Mn are introduced, which is explained by their oxygen-compensating action (21).

After deoxygenation we did not observe the Hall effect in selenium, but the available data (2) lead to the conclusion that deoxygenation is accompanied by a decrease in the concentration by ~ 100 times and in the mobility of current carriers by ~ 10 times.

Fig. 2. Temperature dependence of the electrical conductivity of selenium. 1—initial; 2—deoxygenated; 3-5—oxygenated (at 215°, respectively, for 40, 150, and 350 hours.)

The data cited make it possible to assume that oxygen atoms, being located at the ends of the selenium chain, create acceptor centers, which leads to an increase in the concentration of holes (and consequently to p-type conductivity) and to a decrease in intermolecular barriers, i.e., to an increase in the mobility of the current carriers. This shows that, as in the case of a number of organic polymer semiconductors (22–24), the large scatter of the physical parameters of selenium samples and devices is caused by the method of their preparation, preliminary heat treatment, and measurement (in vacuum, in a gas atmosphere, or in air), which end in different amounts of adsorption or desorption of oxygen atoms.

In conclusion, we express our sincere gratitude to Prof. G. B. Abdullaev, under whose direction this work was carried out, and to Doctor of Physico-Mathematical Sciences M. I. Klinger for valuable advice.

Institute of Physics
Academy of Sciences of the Azerbaijan SSR

Received
23 VII 1965

REFERENCES

1. G. Eckart, Ann. Phys., **14**, 233 (1954).
2. P. T. Kozyrev, FTT, **1**, 113 (1959).
3. G. M. Aliev et al., **6**, 1020 (1964).
4. I. Fakidov, DAN, **63**, 123 (1963).
5. G. B. Abdullaev, D. Sh. Abdinov, G. M. Aliev, Dokl. AN AzerbSSR, No. 3 (1965).
6. L. Nijland, Philips Res. Rep., **9**, 259 (1954).
7. H. W. Henkels, Phys. Rev., **77**, 734 (1950).
8. E. Z. Meilikhov, FTT, **7**, 1743 (1965).
9. H. Gobrecht, A. Tausend, *Physics of Semicond. Proc. of the VII Intern. Confer.*, Paris, 1964.
10. F. Eckart, W. Henrion, H. Peibst, Zs. phys. Chem., **227**, 93 (1964).
11. Ts. N. Nasedov, P. T. Kozyrev, ZhTF, **24**, 2151 (1954).

12. W. E. Spear, Proc. Phys. Soc., **76**, 816 (1960).
13. A. V. Hippel, J. Chem. Phys., **16**, 372 (1948).
14. V. A. Kargin, B. A. Krentsel, *Organic Semiconductors*, Publishing House of the Academy of Sciences of the USSR, 1963, p. 232.
15. A. F. Ioffe, FTT, **1**, 157 (1959).
16. M. I. Klinger, Doctoral dissertation, Sverdlovsk, 1964.
17. R. R. Heikes, W. D. Johnston, J. Chem. Phys., **26**, 582 (1957).
18. J. A. Prins, W. Dekeyser, Physica, **4**, 900 (1937).
19. A. R. Regel, *Structure and Physical Properties of Substances in the Liquid State*, Kiev, 1954.
20. A. I. Gubanov, *Quantum-Electron Theory of Amorphous Conductors*, Publishing House of the Academy of Sciences of the USSR, 1963.
21. S. I. Mekhtieva, G. M. Aliev, D. Sh. Abdinov, Izv. AN AzerbSSR, ser. phys.-mat. and techn. sciences, No. 4 (1964).
22. A. V. Airapetyants, R. M. Voitenko et al., DAN, **148**, 605 (1963).
23. A. G. Vartanyan, Izv. AN SSSR, ser. phys., **20**, 1541 (1956).
24. A. T. Vartanyan, ZhFKh, **31**, 1792 (1957).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.