Soviet-era science, translated into English

ON THE ORIGIN OF HOLE CONDUCTIVITY IN SELENIUM

PHYSICS

1970

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-197001.16024

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

Figure 1. Dependence of the thermoe.m.f. (1) and electrical conductivity (2) of amorphous selenium on the content of the crystalline phase

Figure 1: Figure 1. Dependence of the thermoe.m.f. (1) and electrical conductivity (2) of amorphous selenium on the content of the crystalline phase

Abstract

Full Text

UDC 537.311.1

PHYSICS

Academician of the Academy of Sciences of the Azerbaijan SSR G. B. ABDULLAEV, G. M. ALIEV, S. I. MEKHTIEVA,
G. G. MAMEDALIEVA, F. B. GADZHIEV, N. Z. DZHALILOV, D. Sh. ABDINOV

ON THE ORIGIN OF HOLE CONDUCTIVITY IN SELENIUM

The mechanism of p-conductivity in selenium, which is an elementary classical semiconductor, has still not received a definitive explanation. In works ($^{1-4}$) it is assumed that oxygen atoms in selenium, by creating acceptor levels, determine its hole conductivity. However, direct data confirming this assumption are almost absent.

Taking into account that impurities in the amorphous state are inactive and that their activation occurs during crystallization of the substance (^{5}), the aim of the present work was to obtain information on the origin of the hole conductivity of selenium and to clarify the possibility of obtaining selenium with electronic conductivity by studying the type of conductivity of amorphous selenium with different degrees of crystallinity, as well as of single-crystalline selenium before and after deoxygenation.

Fig. 1. Dependence of the thermoe.m.f. (1) and electrical conductivity (2) of amorphous selenium on the content of the crystalline phase

Amorphous samples were obtained by rapid cooling of molten selenium in vacuum, and single crystals according to (^{6}). Crystallization of amorphous samples was carried out at 100° for 10, 20, 30, 40, 60, 120, and 180 min, and the degree of crystallinity after each heat treatment was determined by the method of (^{7}). The obtained values of electrical conductivity and thermoe.m.f. are equilibrium values (^{8},^{9}).

Figure 1 shows the dependence of the thermoe.m.f. and electrical conductivity of amorphous selenium on the content of the crystalline phase in it. It is seen that

SovietRxiv

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

amorphous selenium at room temperature is of the n-type of conductivity, but after $\sim 10\%$ crystallization it becomes hole-conducting. In addition, the change in the type of conductivity occurs when the value of the electrical conductivity exceeds the value $\sigma \approx 6 \cdot 10^{-11}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, i.e., samples of amorphous selenium possessing an electrical conductivity smaller than $\sim 6 \cdot 10^{-11}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ have n-conductivity, and those with a conductivity greater than $\sim 6 \cdot 10^{-11}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ have p-conductivity.

The electrical properties of selenium are not connected with the presence of lattice periodicity, but are determined mainly by short-range order. Therefore it is precisely the short-range order that determines the width of the forbidden band and, consequently, the concentration of intrinsic free electrons and holes. However, upon amorphization of the substance there occurs such a grouping of atoms around defects that impurities active in the crystalline state become inactive in the amorphous state (or, at least, the action of impurities is weakened). On this basis it may be assumed that, like other amorphous substances (^{5}), amorphous selenium with a low impurity concentration is an intrinsic semiconductor, and in it the hole concentration n_h will be equal to the electron concentration n_e. Since the electron mobility u_e in amorphous selenium is ~ 2 times greater than the hole mobility u_h ($u_\mathrm{e} = 0.32;\ u_\mathrm{h} = 0.14\ \mathrm{cm}^2/\mathrm{sec}$, (^{10})), in amorphous selenium $n_\mathrm{e} u_\mathrm{e} > n_\mathrm{h} u_\mathrm{h}$, which determines its n-type conductivity.

As noted above, during the gradual transition of selenium from the amorphous phase to the crystalline phase, impurities that are inactive in the amorphous state become active in the crystalline state (^{5}), and the concentration of holes in selenium predominates over the concentration of electrons. This occurs due to the predominance of acceptor impurities, mainly oxygen impurities ($^{3,\ 4}$), which leads to a change in the type of conductivity from electronic to hole. The data presented on the dependence of the type of conductivity of selenium on the degree of crystallinity make it possible to obtain selenium samples with a controllable type of conductivity.

Fig. 2. Temperature dependence of the electrical conductivity of hexagonal selenium.
1, 3—dark conductivity of non-oxygenated (1) and oxygenated (3) selenium; 2, 4 –conductivity of non-oxygenated (2) and oxygenated (4) selenium under illumination

Fig. 3. Temperature dependence of the thermoelectric e.m.f. coefficient of

hexagonal selenium.
1, 3—non-oxygenated (1) and oxygenated (3) selenium in the dark; 2, 4—non-oxygenated (2) and oxygenated (4) selenium under illumination

In Figs. 2 and 3 the results of measurements on single-crystalline selenium are presented. It is seen that the dark electrical conductivity of non-oxygenated selenium increases with temperature with an activation energy of ~ 0.1 eV. After illumination, the electrical conductivity increases at ~ 170°K by ~ 100 times, and its temperature behavior has a different character—with increasing temperature σ of selenium decreases.

The temperature dependence of α for non-oxygenated selenium before and after illumination indicates that both the change in values (under illumination) and the exponential temperature dependence of the electrical conductivity are due to the mobility of the current carriers, while the concentration of the latter remains almost unchanged.

The temperature dependence of the dark and light electrical conductivity of oxygenated selenium has almost the same character, with the only difference that the values of the dark σ are 5–6 times lower than the light values.

An interesting result is obtained when measuring the temperature dependence of the thermoelectric e.m.f. coefficient α of oxygenated selenium before and after

illumination. At low temperatures (up to 230°K) the thermoelectric-power coefficient indicates electronic dark conductivity, which changes to hole conductivity above ~ 230°K (Fig. 3, 3). Under illumination, the type of conductivity over the entire measured temperature interval corresponds to hole conductivity, while the thermoelectric power decreases only slightly with temperature (Fig. 3, 4).

As was indicated above, the main acceptor centers in pure selenium are oxygen impurities, whose concentration is $\sim 5 \cdot 10^{18}$ cm^{-3}. Apparently, when selenium is purified of oxygen impurities, the hole concentration drops sharply and at 130°K becomes comparable with the electron concentration. The negative sign of the thermoelectric-power coefficient up to ~ 230°K indicates that in this temperature interval, in single crystals of deoxygenated selenium, $n_{\mathrm{e}}u_{\mathrm{e}} > n_{\mathrm{h}}u_{\mathrm{h}}$. Apparently, in deoxygenated selenium single-crystal samples there are shallow acceptor levels that are not completely ionized at 130°K. As the temperature rises, they become ionized, leading to an increase in the hole concentration, and, consequently, σ, and above ~ 230°K $n_{\mathrm{h}}u_{\mathrm{h}}$ becomes greater than $n_{\mathrm{e}}u_{\mathrm{e}}$. Under the action of light, some of the above-mentioned shallow acceptor levels, again becoming ionized, lead to an increase in the hole concentration and, consequently, to an increase in electrical conductivity and to a change in the sign of the thermoelectric power. In illuminated samples of deoxygenated selenium, ionization of shallow acceptor levels continues with temperature, which accounts for the increase in electrical conductivity and for a certain decrease in the thermoelectric-power coefficient with temperature.

One might suppose that under illumination the hole mobility in deoxygenated selenium increases faster than the electron mobility, which leads to $n_{\mathrm{h}}u_{\mathrm{h}} > n_{\mathrm{e}}u_{\mathrm{e}}$. In that case, however, the invariability of the activation energy of the electrical conductivity under illumination (as in the case of non-deoxygenated selenium) and the saturation of the curves of the temperature dependence of the light and dark electrical conductivity of deoxygenated selenium would be incomprehensible.

Upon deoxygenation of polycrystalline hexagonal selenium, the electrical conductivity at a given temperature decreases by ~ 1000 times ([2,4]), i.e., by ~ 100 times more than in the case of single-crystal selenium. This is apparently due to two factors: a) when selenium single crystals are obtained, they are purified of oxygen impurities; b) oxygen atoms in polycrystalline samples, by reducing the intermolecular potential barriers, lead to an increase in the mobility of current carriers as they move ([5]).

Since in single-crystal selenium samples the chain length is much greater than in polycrystalline ones (in the ideal case, the chain length of a single crystal is equal to the length of the sample), the number of free ends and, correspondingly, the concentration of intermolecular barriers are much smaller than in polycrystals. Therefore, in this case no noticeable influence of oxygen impurities on the mobility of current carriers is observed.

The change in the electrical properties of selenium single crystals upon deoxygenation indicates that oxygen atoms enter the selenium lattice.

Institute of Physics
Academy of Sciences of the Azerbaijan SSR
Baku

Received
12 III 1970

CITED LITERATURE

1. G. B. Abdullaev, G. M. Aliev, FTT, 6, 1020 (1964).
2. G. B. Abdullaev, S. I. Mekhtieva et al., Fiz. tekhn. poluprovodnikov, 1, 519, 1967.
3. G. M. Aliev, D. Sh. Abdinov et al., DAN, 167, 782 (1966).
4. G. B. Abdullaev, S. I. Mekhtieva et al., Phys. Stat. Solid., 11, 891 (1965).
5. A. I. Gubanov, *Quantum-Electronic Theory of Amorphous Conductors*, Publishing House of the Academy of Sciences of the USSR, 1963.
6. G. M. Aliev, N. Z. Dzhalilov, Izv. AN AzerbSSR, ser. fiz.-tekhn. i matem.

nauk, 4, 79 (1964).

7. S. I. Mekhtieva, D. Sh. Abdinov, G. M. Aliev, ZhTF, 42, 270 (1968).
8. Yu. Kadel, ZhETF, 24, 6 (1953).
9. P. T. Kozyrev, ZhTF, 26, 265 (1956); 27, 35 (1957).
10. W. E. Spear, Proc. Phys. Soc., 86, 826 (1960).

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

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