Electrical conductivity of MoS$_2$ thin films and graphite under continuous injection to protons

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Abstract. The electrical conductivity of thin films of MoS$_2$ and graphite has been studied under conditions of continuous injection of low-energy protons ($\sim$ 1-4 keV). The effect of a sharp increase (by 3-4 orders of magnitude) in the electrical conductivity of substances with a layered structure (MoS$_2$ and graphite) at $T \sim 293$ K has been established. The observed effect increases (from 2 to 10 times) as the temperature decreases from room temperature to liquid nitrogen temperature ($T \sim 77$ K) and with increasing number of protons injected into the sample. The established temperature variation of electrical resistance is typical for materials with a metallic type of conductivity. It is shown that a thin surface layer, onto which protons penetrate, is responsible for the change in the electrical conductivity of MoS$_2$ and graphite films.

Introduction

It is well known that graphite and molybdenum disulfide are compounds with a layered structure. Compounds with such structures are composed of different layers that are linked together by weak der Waals forces. In the interlayer space between the atoms of alkali metals (Li, Na), the intercalating compounds of such compounds can be changed. It is known that the intercalation of MoS$_2$ with alkali metals leads to the appearance of superconductivity ($T_k \sim 8$-$10$ K) [1].

Hydrogen in the structure of the outer electron shell is similar to alkali metals. Initially, it was assumed that the intercalation of MoS$_2$ with hydrogen can lead to a significant change in its electrical resistance. Our studies have shown [2] that upon intercalation of MoS$_2$ with hydrogen, its electrical resistance changed not in the direction of decreasing, but increasing. However, under continuous injection of ionized conditions of hydrogen (protons) into the film semiconductor MoS$_2$, a significant increase in electrical conductivity was observed [3].

In this work, we have analyzed the electrical conductivity (at room and liquid nitrogen temperatures) of a compound with a layered structure: film semiconductors MoS$_2$ and graphite under conditions of continuous injection of low-energy protons ($\sim$ 1-4 keV).

Research methods and objects

To create a continuous flux of protons injected into the sample under study, we used a stationary ion source (IS) with a cold cathode and a magnetic field that forms an ion beam of relatively low intensity (Figure 1), similar to that used in paper [3]. The electric current in the ion beam was $\sim$ 0.2-1.2 mA, accelerating the potential difference from 500 to 4000 volts. The residual pressure in the chamber, before the injection of hydrogen $\sim$ 10-6 mm Hg, when the source is operating, the pressure rises to $10^{-4}$-$10^{-3}$ mm Hg. (due to the injection of hydrogen into the chamber). Hydrogen is ionized by primary electrons
when voltage is applied to the anode. Subsequently, the discharge is supported by secondary electrons generated in the process of gas ionization. According to our estimates, at a hydrogen pressure of (1-3) • 10^{-3} mm Hg, the ion current density is \( \sim 0.01 \text{ mA/cm}^2 \), and the ionization of the hydrogen beam is \( \sim 80\% \).

The objects of study were thin films of semiconductor MoS\(_2\) and graphite, obtained on the surface of polished substrates (30x40 mm) made of glass or quartz by the mechanical rubbing of the powder into the rough surface of dielectrics. The topography of the ground surfaces and the electrical contacts formed on the films were similar to those described in the source [3].

The electrical resistance of the initial samples was measured using an E6-13 terahmmeter with a measurement error of \( \sim (3-10)\% \).

For an accurate assessment of the electrical conductivity of high-resistance (\( \sim 10^{10} - 10^{11} \text{ ohm} \)) film samples in the process of continuous proton injection, a special compensation electrical circuit was used, similar to that described in [3]. It made it possible to fix electrical resistances from \( 10^5 \) to \( 10^7 \Omega \), with an error of \( \sim (30-35)\% \), taking into account the "parasitic" EMF (electromotive force).

Results

Studies of the electrical conductivity of glass and quartz substrates at room temperature (293 K) and liquid nitrogen temperature (\( \sim 77 \text{ K} \)) showed that with continuous injection of protons, their electrical resistance remained above \( 10^7 \text{ ohms} \). This made it possible to use glass and quartz as a "material" of substrates in studying the electrical conductivity of thin films of MoS\(_2\) and graphite under conditions of continuous proton injection.

When carrying out an experiment on the effect of injection of low-energy protons on the electrical conductivity of semiconductor MoS\(_2\) films, we used a glass (as the most accessible) dielectric substrate 30x40 mm in size, the electrical resistance of which before the action of protons and during their continuous injection was several orders of magnitude (or at least an order of magnitude) higher than for the investigated film samples of MoS\(_2\). This excluded the shunting of the MoS\(_2\) semiconductor film by the substrate during measurements.

It follows from Table 1 that, under conditions of continuous proton injection, the resistivity of MoS\(_2\) films decreases by 4-5 orders of magnitude at room temperature (\( T \sim 293 \text{ K} \)) and from 2 to 10 times upon cooling the samples to \( T \sim 77 \text{ K} \).

On the surfaces of rough quartz plates with a size of 30x40mm, by rubbing graphite, films with electrical resistance were formed: \( 3.0 \times 10^9 \Omega; 1.5 \times 10^8 \Omega; 1.5 \times 10^7 \Omega \) (Table 2). In the used set of graphite films with electrical resistivity in the range from \( 10^9 \) to \( 10^7 \text{ ohms} \), their thickness varied by
about 100 times. We did not directly control the thickness of the graphite films, but evaluated it qualitatively, bearing in mind that the electrical resistance of the film is inversely proportional to its thickness.

Table 1. Electrical resistance of dielectrics and film semiconductor MoS$_2$ in the process of continuous exposure to them with low-energy protons

| No. | Material | Electro resistance of sample (R, $\Omega$), T~293 K | Electro resistance of sample in the process of protons exposure (R, $\Omega$), T~293 K | Electro resistance of sample after process of protons exposure (R, $\Omega$), T~293 K |
|-----|----------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1   | MoS$_2$  | $(3.0\pm0.2)\cdot10^{10}$                   | $(3\pm1)\cdot10^{7}$                          |                                            |
| 2   | MoS$_2$  | $(7.0\pm0.2)\cdot10^{10}$                   | $(3\pm1)\cdot10^{6}$                          | $(3.0\pm0.2)\cdot10^{11}$                   |
| 3   | MoS$_2$  | $(3.0\pm0.2)\cdot10^{11}$                   | $(6\pm2)\cdot10^{6}$                          | $(3\pm1)\cdot10^{6}$                        |
| 4   | MoS$_2$  | $(8.0\pm0.2)\cdot10^{11}$                   | $(6\pm2)\cdot10^{6}$                          | $(3\pm1)\cdot10^{6}$                        |

Table 2. Electrical resistance of graphite films (of different thickness) on a quartz substrate at the same current strength of the ion source.

| №  | Electrical resistance of the original sample, $\Omega$ (T~293 K) | Sample electrical resistance during exposure to protons, $\Omega$ (T~293 K) | (T~77 K) |
|----|-------------------------------------------------------------|-------------------------------------------------------------------------|----------|
| 1  | $(3.0\pm0.2)\cdot10^{10}$                                  | $(2.0\pm0.0)\cdot10^{7}$                                              | $(6.0\pm1.5)\cdot10^{6}$ |
| 2  | $(1.5\pm0.1)\cdot10^{10}$                                  | $(1.0\pm0.3)\cdot10^{7}$                                              | $(5.0\pm1.5)\cdot10^{6}$ |
| 3  | $(1.5\pm0.1)\cdot10^{10}$                                  | $(9\pm2)\cdot10^{6}$                                                  | $(1.3\pm0.4)\cdot10^{6}$ |

Discussion of the results

An increase in the electrical conductivity of MoS$_2$ (by 4-5 orders of magnitude) under conditions of continuous injection of low-energy protons (~ 1-4 keV) means that protons have penetrated into the surface layer of the sample (to a depth of ~ $10^{-6}$ m or less) as well as the fact that In the surface layer of the sample, additional uncompensated carriers of electric current appeared, whose concentration exceeded the concentration of free electrons. According to the data given in Table 1, regardless of the initial value of the electrical resistance of the MoS$_2$ sample, its value during the injection of protons is approximately the same and amounts to ~ $(3-6)\cdot10^{6}\ \Omega$. This suggests that only a thin surface layer, into which protons are injected, is responsible for the change in the electrical conductivity of MoS$_2$ film samples. Based on the increase in the electrical conductivity of the sample, it is reasonable to assume that the carrier concentration in the surface layer of semiconductor MoS$_2$ increases by several orders of magnitude when we inject protons into the sample. It follows from Table 1 that, under conditions of continuous proton injection, the electrical resistance of MoS$_2$ samples decreases from 2 to 10 times when cooled from room temperature to the temperature of liquid nitrogen. It is important that such a temperature variation of electrical resistance is characteristic of materials with a metallic type of conductivity.

The layered structure of MoS$_2$ favorably affects both the penetration of protons into the surface layer and their further movement along the sample surface. It was shown in [1] that hydrogen atoms can be located in the interlayer space of MoS$_2$ and lead to a change in its properties. Apparently, new charges that appear in the surface layer of MoS$_2$, upon injection of protons, can move through these interlayer spaces "tunnels".

Graphite, like MoS$_2$, has a layered structure, and the behavior of its electrical conductivity during the continuous injection of protons (Table 2) is in many respects similar to that observed in the case of MoS$_2$ (Table 1). However, graphite has its own characteristics. The fact is that the layered structure of graphite
affects its electrical conductivity: in the direction of the parallel layers, it is of the metallic type in the
direction perpendicular to the semiconductor. The specific electrical resistance of graphite in the
polycrystalline state is $\sim 8 \cdot 10^{-6} \, \Omega \cdot m$, i.e. it occupies a certain intermediate position between
semiconductors and metals [4].

The results of studying the electrical resistance of graphite films in the course of continuous proton
injection at temperatures of $\sim 293 \, K$ (room temperature) and $\sim 77 \, K$ (liquid nitrogen) are presented in
Table 2. The samples were specially prepared so that their initial electrical resistances differed by an
order of magnitude. The current strength of the ion source was $\sim 0.2 \, mA$. It follows from Table 2 that
the electrical resistivity of the films decreased to a value of $\sim 10^7$ ohms (at $T \sim 293 \, K$) and from 2 to 10
times when the temperature ($\sim 77 \, K$) was reached, and these changes practically did not depend on the
electrical resistivity of the initial sample. This suggests that for all studied graphite films only a thin
surface layer works, and practically nothing depends on the thickness of the film itself. In this case, the
electrical resistance of the graphite film is determined simply by the number of protons supplied to the
sample during injection. This is evidenced by the established dependence of the electrical resistance (R)
of a graphite film at ($T \sim 293 \, K$), under conditions of continuous injection of protons into it, on the
current strength of the ion source (Figure 2). It follows from the figure that the value of (R) decreases
with increasing current strength of the ion source. This can be explained by the fact that the number of
carriers of electric current in the sample increases with an increase in the number of injected protons.

Thus, regardless of the electrical resistance of the initial graphite sample, its electrical resistance in
the process of continuous proton injection was practically the same; as in the case of MoS$_2$ films, only
a thin surface layer into which protons penetrated "worked".

![Figure 2. Electrical resistance of a graphite film at room temperature ($T \sim 293 \, K$), under conditions of
continuous injection of protons into it, on the magnitude of the ion source current](image)

**Conclusion**

1. The effect of a sharp increase in the electrical conductivity of substances with a layered structure
(MoS$_2$ and graphite) in the film state as a result of the penetration of continuously injected low-energy
protons ($\sim 1-4 \, keV$) into the surface layers has been established.
2. The observed effect is enhanced as the temperature decreases from room temperature to the liquid
nitrogen temperature and with increasing number of protons injected into the sample, which is
characteristic of materials with the metallic type of conductivity.
3. It was found that, whatever the electrical resistance value of the initial sample (MoS$_2$ or graphite), its
electrical conductivity during proton injection is approximately the same. This suggests that, for all
studied films, only a thin surface layer, into which protons penetrate, "works".

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References

[1] Gamble F R et al 1970 Science 168 568
[2] Burkhanov G S, Lachenkov S A, Kononov M A, Vlasenko V A, Mikhailova A B and Korenovskiy N L 2017 Perspectivn Mater 1 54-60
[3] Burkhanov G S, Lachenkov S A, Kononov M A 2018 DAN 481 2 1-4
[4] Shulepov S V 1990 Physics of Carbon-Graphite Materials (Moscow Metallurgiya) Edition 2. p 336