Change of electrical conductivity of MoS₂ under exposure to protons

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Abstract. A significant drop (by a factor of 10,000) in the electrical resistance of the thin-film semiconductor MoS₂ with continuous injection of protons into it under conditions of established dynamic equilibrium was found. With the cessation of proton injection, the effect disappears. These films MoS₂ were obtained on polished glass supports by means of mechanical friction of powder into a rough surface. In order to create a permanent proton flow directed to the sample plasma ion source with cold cathode was used.

1. Introduction

Recently we had studied the influence of Hydrogen ions influence on the properties of FeSe and MoS₂ by usage of ion source (IS) [1]. It was stated that after the Hydrogen (proton) injection, electrical resistance of MoS₂ was increasing by times, but mass of the sample had increased.

Recently Japanese physicists published a work [2] showing that MoS₂ films doped with electrons obtain superconducting properties with Tc ~ 10.5 K while reaching the optimal value of electrical charge in the sample.

From that point of view, it seemed interesting for authors to find out how would change the electrical resistance of MoS₂ if the sample would be doped with protons instead of electrons in the conditions of permanent flow of protons directed to the sample.

Abovementioned scenario might be realized if the protons supplied from ion source to the MoS₂ sample until the dynamic steady-state conditions are set and carried on further.

Since there is only a small amount of free electrons in the molybdenum disulphide (MoS₂), those electrons could not neutralize all supplied protons (to Hydrogen atoms). Thus, change of sample electrical conductivity type from semiconductive to metallic type is possible.

Purpose of this work is to research the change of electrical conductivity of MoS₂ sample under permanent doping of the sample by protons using the ion source (IS) under conditions of steady-state dynamic equilibrium.

2. Experiment methodic

To perform the test thin films of MoS₂ were used. These films were obtained on polished glass supports by means of mechanical friction of powder into a rough surface. In our case typical surface roughness of glass was around 2-3 μm. Surface structure of supports with deposited MoS₂ films was analyzed on the atomic-force microscope P4-SPM–MDT. Section analysis of support unit filled with MoS₂ shows that maximum roughness height is below 205 nm and roughness depth is below 165 nm. Thus, difference between maximum and minimum peak-to-valley value is around 40 nm.

Taking into consideration that distance between layers along the axis “c” into MoS₂ sample is around 1.2 nm, film thickness difference along the sample surface lies between 30-35 monolayer. According to reference data, specific electrical resistivity (ρ) of massive sample of MoS₂ is MoS₂ ~ 10⁵ Ohm·m. Considering that MoS₂ film electrical resistivity value equals (2 ± 0,1)·10¹⁰ Ohm, film effective thickness could be calculated, which according to the calculation equals ~ 5·10⁻⁶ m.
On the MoS$_2$ films prepared by abovementioned technique two silver stripes were deposited with thin copper conductors fastened to the stripes by the means of conducting silver glue.

In order to create a permanent proton flow directed to the sample plasma ion source with cold cathode was used. This ion source is equipped with cylindrical form constant magnets, which are placed around cylindrical anode. Constant magnets create an axial magnetic field in order to decrease the plasma area and increase the ionization rate per electron. High efficiency of the selected scheme allowed reaching the necessary operating parameters of ionic source. All measurements were made in different variations of following operation conditions of the system: produced particles flux ionization rate:

$$\gamma = \frac{N_i}{N_i + N_A} \approx 0.85$$

Hydrogen pressure $(1-3) \cdot 10^{-2}$ Pa, ionic current density $\sim 0.01$ mA/cm$^2$.

In general, in ion source plasma several simultaneous processes could be observed: Hydrogen molecules dissociation, energization and dissociation by electron impact and other processes [3]. Relative proportion of abovementioned transformations in plasma depends on the ion source (IS) type and operation regimes. During the operation of our ion source (due to its specific design) single-stage process of electron collision with Hydrogen molecule had prevailed. The main reactions were following:

\[
\begin{align*}
H_2 + e &= H_2^+ + 2e \\
H_2 + e &= H_2^+ + H_1 + 2e
\end{align*}
\]

Schematic image of the system for permanent supply of Hydrogen ions to the surface of MoS$_2$ film is shown in fig. 1. Test was performed in a vacuum chamber. Air was pumped out from the chamber. Pressure inside the chamber was $\sim 5 \cdot 10^{-4}$ Pa. Support with MoS$_2$ film was placed on a glass table with current-consuming electrodes mounted on a glue. Ion source is situated in 5 cm from the support. Hydrogen ions energy was around 4000 eV.

![Figure 1. Scheme of an electron impact ion source.](image)

As was mentioned above, the experiment was aimed at examining the variation of the MoS$_2$ film conductivity (fig. 2) under continuous injection of protons from the IS. It should be noted that the MoS$_2$ film subjected to the proton flux became positively charged. A special compensating circuit was used to factor in the emergence of parasitic EMF ($\sim 15$ V) and thus obtain an accurate estimate of the conductivity of the film sample. The presence of this EMF makes it impossible to determine the resistivity of a thin
film using a certain common technique (e.g., teraohmmeter measurements) and necessitates the introduction of more complex measurement circuits. The compensating circuit used is presented in fig. 2, where $E_{\text{ext}}$ is the external source with EMF = 7.0 V, $R_g$ is the added resistance ($4 \times 10^3 \, \Omega$), $\mu A$ is the microammeter with a full-scale current of 100 $\mu$A and an accuracy of 0.5 $\mu$A, $R_u$ is the resistance of the sample studied subjected to the proton flux, $E_{\text{per}}$ is the parasitic EMF, and DS is the double EMF direction switch. Since the internal resistances of the EMF source and the microammeter are much lower than $R_g$, they were neglected in calculations.

![Electrical circuit for the measurement of resistivity of thin MoS$_2$ films subjected to the proton flux.](image)

The current strength was measured to be $I_2$ and $I_1$ in two positions of the EMF direction switch. The resistance of the studied sample was then calculated based on the results obtained in accordance with the following formula:

$$R_u = \frac{2 \cdot E_{\text{ext}} - (I_2 - I_1) \cdot R_g}{I_2 - I_1}$$

The sample resistance calculated with the parasitic EMF and the experimental error factored in was $(3.1 \pm 0.8) \times 10^6 \, \Omega$. This value is approximately four orders of magnitude lower than the resistance of the as prepared MoS$_2$ film. Arguably, the resistivity did also decrease by 3–4 orders of magnitude to $10^1$–$10^2 \, \Omega\,m$.

3. Discussion of results
Tests showed that change in MoS$_2$ film electrical resistance related to appearance of additional free charges in the sample. Quite possibly that during the interaction between protons and MoS$_2$ sample, electrons might have been knocked out and besides protons positively charged “holes” could have appeared in the film. Important to note, that electrical resistance of MoS$_2$ sample decreases under the influence of protons. Thus not all positive charge carriers are being neutralized. In order to accurately define composition of carriers, which abruptly increase electrical conductivity of the sample, number of additional fine experiments should be performed. However influence of protons is in no doubt. Additional evidence of protons presence is significant increase of sample mass after the radiation process, which was previously described in [1].

It is known that carriers concentration into semiconductors equals $\sim 10^{16} \, m^{-3}$, however carriers concentration in metals equals $\sim (10^{28} - 10^{29}) \, m^{-3}$. In first iteration electrical conductivity ($\sigma$) could be expressed as:

$$\sigma = \frac{n \cdot e^2 \cdot \tau}{m}$$
where $\sigma$ – electrical conductivity; $e$ – elementary charge; $\tau$ – mean free time; $m$ – carrier mass.

Taking into consideration that electrical conductivity of the sample during the radiation process had been increasing approximately $10^4$ times, and proton mass is $10^3$ times higher than electron mass, and assuming that $\tau$ is relatively constant, it could be considered that carriers concentration increases in at least $10^4$ times.

4. Conclusion

For the first time ever effect of MoS$_2$ film-type semiconductor electrical conductivity increase (by a factor of 10,000) was experimentally discovered under permanent doping of the sample by protons in conditions of steady-state dynamic equilibrium. Effect disappears as proton influence stops. Possibly new unexplored effects would be discovered during further investigation of this problem. Performance of current investigations became possible due to the development of new methods of MoS$_2$ thin film production and original methodic of films electrical conductivity determination during the protons radiation process.

References

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