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Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2024 Project Summary

1. Student name & home university: Gergő Németh from Budapest University of Technology and Economics

2. ND faculty name & department: Professor László Forró, Dr. Bence Márkus, Dr. Anna Nyáry, Stavropoulos Center for Complex Quantum Matter, Department of Physics and Astronomy

3. Summer project title: Pursuing superconductivity in doped transition metal dichalcogenides

4. Briefly describe new skills you acquired during your summer research:

During my summer research, I acquired several new laboratory skills. I learned to work in a glove box under an inert argon atmosphere. I became proficient in using a flame torch to shape quartz tubes, for custom experimental setups. I handled various chemicals and equipment, including preparing an ionic gel and performing chemical doping processes. I used tube furnaces for vapor-phase doping and pressure holder reactors for liquid-phase doping. I also gained experience with an ARS Cryocooler capable of reaching temperatures as low as 4 K. My work required precise soldering under a microscope, working with gold wires that were only 50 micrometers thick to create electrical contacts. I gained fundamental knowledge in photolithography and microfabrication.

5. Briefly share a practical application/end use of your research:

The development of p-type doped Transition Metal Dichalcogenides could lead to the creation of superconducting materials stable under ambient conditions. These are crucial for advanced technologies like spintronics, next-generation computer architectures, and energy storage solutions.

6. 50- to 75-word abstract of your project:

This project aimed to explore the possibility of achieving superconductivity in transition metal dichalcogenides (TMDCs) through p-type doping. The research involved chemical doping and ionic gating techniques to alter the electronic properties of WSe_2 and MoS_2 crystals. Initial results showed promising structural changes and gradual changes in their electric resistance, though further work is required to confirm the success of intercalation and to achieve superconductivity.

7. References for papers, posters, or presentations of your research:

Presentation: 08.02.2024. NDnano Research Reviews

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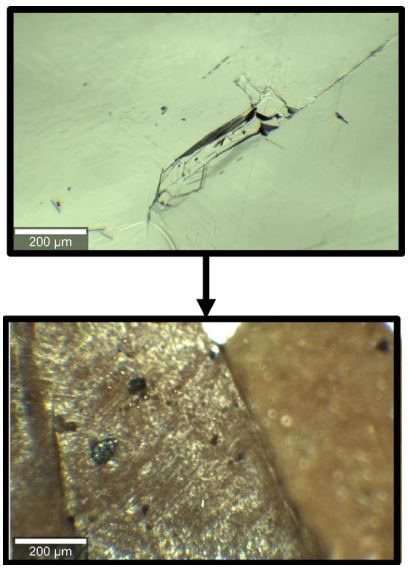
One-page project summary that describes problem, project goal and your activities / results:

Transition metal dichalcogenides (TMDCs) are a widely studied material family. Previous research has demonstrated that these semiconductors can be converted into metals or even superconductors through n-type doping. The challenge with n-type doping is that the resulting products are often air-sensitive. Meanwhile, p-type doping has not yet been thoroughly explored. The motivation for p-type doping was given by theoretical colleagues who suggested that p-type doping might produce more stable products with an even more robust superconducting phase.

My summer project aimed to investigate the possibility of achieving p-type doping in TMDCs, specifically WSe_2 and MoS_2, and to explore their potential for superconductivity. To achieve this, I explored two primary methods: chemical doping and ionic gating (electric field doping).

In the first approach, chemical doping was achieved by using metal chlorides as high-electron-affinity dopants, with the aim of intercalating these molecules into the interstitial spaces of the lattice. Solid dopants, such as $FeCl_3$, $AlCl_3$, $RuCl_3$, and $CuCl_2$, were used in vapor-phase intercalation experiments. In these reactions, I placed the dopant and the pristine sample at opposite ends of a quartz tube with a narrowing in the middle. The quartz tubes were then placed in tube furnaces, where the dopant vapor's chemical potential gradient drove the doping reaction. The reactions of liquid dopants, such as $SbCl_5$, $SnCl_4$, and Br_2 were performed by soaking the pristine samples in the dopants inside closed pressure reactor vessels. These vessels were then heated to create higher temperature and pressure conditions, facilitating better reaction outcomes.
For most of the chemical doping reactions, the dopants were prepared in a glove box under an inert argon atmosphere to avoid reactions between the chlorides and the moisture of the air. I performed at least 20 of these doping reactions, each of which took 1 to 5 days to complete.

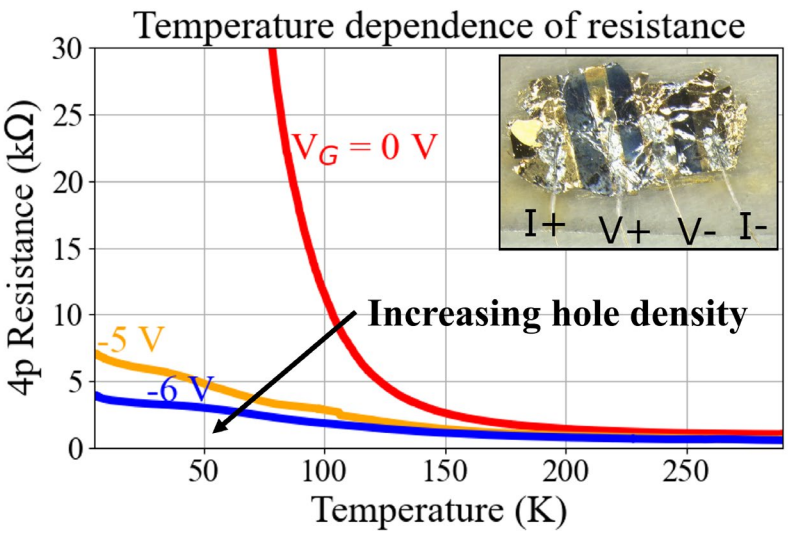


1. Figure Discoloration after intercalation. Microscopic images of the pristine sample (top) and the $RuCl_3$-doped sample (bottom).

For the characterization of the doped samples, I used Raman spectroscopy, an optical technique for studying the vibrational modes (phonons) of materials. This method was chosen because intercalation-induced changes in the lattice structure can introduce new vibrational modes that are detectable in the Raman spectra.
I conducted several Raman measurements and, by comparing the spectra of the pristine materials with those of the doped products, I observed some promising results, particularly in the samples doped with $RuCl_3$, $AlCl_3$, and Br_2. The position of certain peaks shifted, and new peaks appeared in the spectra. Additionally, I noticed some discoloration on the samples after the reactions. These observations suggest that the intercalation process seems to have been successful but additional measurements are required to confirm.
The next step in the characterization is to perform electric transport and Hall measurements, to measure the conductivity and the charge carrier density of the samples. My results provide a solid foundation for continuing this project in the future.

In the second method, ionic gating was used to adjust the charge carrier density in pristine TMDC samples using an external electric field. This approach utilized ionic gel and gold electrodes for gating. The ionic gel is a composite material consisting of an ionic liquid immobilized

in a polymer matrix. Initially, I optimized the ionic gel recipe and standardized the preparation process. The gel was then applied between a small flake of the sample and the gate electrode. When a gate voltage was applied, the electronic dipoles in the ionic liquid aligned with the electric field, creating an electronic double layer at the gel-sample interface. This setup generates a higher electric field at the interface than conventional metal-oxide gating and leads to enhanced charge carrier injection into the material.
Before applying the ionic gel, I contacted the TMDC flakes for four-point probe resistivity measurements using gold wires with a diameter of 50 micrometers. The field-effect transistor-like samples were then placed in a vacuum cryocooler for transport measurements.
Firstly, the resistance of the samples was examined as a function of gate voltage at room temperature. A significant decrease in resistance with applied gate voltage was observed, indicating an increased density of charge carriers. In these measurements, the negative gate voltage region corresponds to p-type doping or hole injection.
After successful gating, the proper gate voltages can be determined for the temperature-dependent resistance measurements from room temperature down to cryogenic temperature.



2. Figure The temperature dependence of the resistance of a WSe_2 flake (upper-right corner) under different gate voltages.

The temperature dependence of the resistance serves with information about the metallicity of the material. For example, without gating, the resistance increases significantly with decreasing temperature, which is the typical behavior of semiconductors. However, with gate voltage applied, I observed that the extent of resistance increase with decreasing temperature was notably smaller, indicating an increased charge carrier density. Despite these promising results, metallic behavior (decreasing resistance with decreasing temperature) was not observed. We hypothesized that sample thickness might be an issue and planned to further develop this method using microfabricated samples. We created photolithographed circuits for applying the gate voltage and contacting exfoliated 50-200 nm thick TMDC samples. At this point, we encountered an issue where the contacts were not functioning due to a lack of back-gating, resulting in huge contact resistance between the exfoliated sample and the metal electrodes. Future work on this project should focus on improving the microfabrication process, as this technique is expected to enhance the efficiency of gating and also enable transport and Hall measurements on the tiny flakes of chemically doped samples.