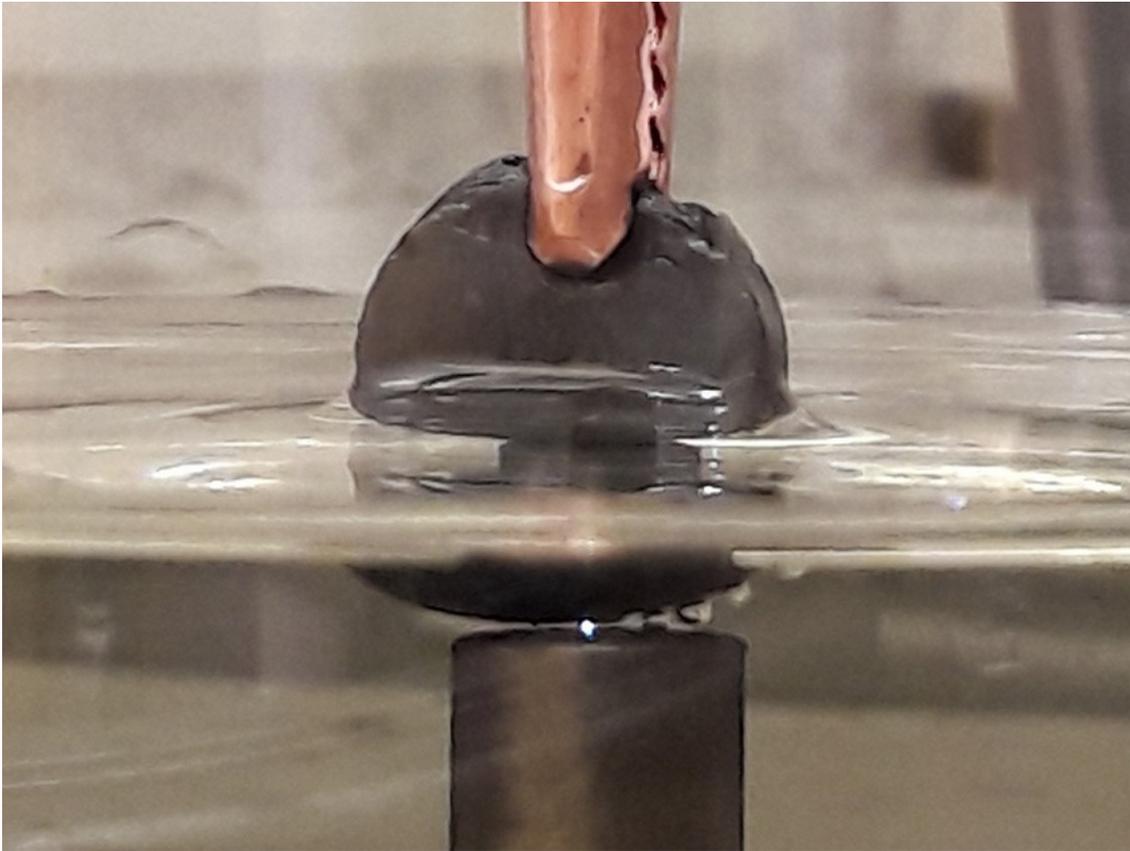




**CHALMERS**  
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# **Investigation of two dimensional material production with spark erosion**

An investigation of the possibility to produce two dimensional nanoflakes for electronic applications

Master's thesis in Nanotechnology

**EMELIE LINDGREN**

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Department of Microtechnology and Nanoscience  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2017



MASTER'S THESIS 2017

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EMELIE LINDGREN



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

Department of Microtechnology and Nanoscience  
*Electronics Materials and Systems Laboratory*  
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tronic applications  
EMELIE LINDGREN

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Supervisor: Yifeng Fu, Department of Microtechnology and Nanoscience  
Examiner: Johan Liu, Department of Microtechnology and Nanoscience

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Department of Microtechnology and Nanoscience  
Electronics Materials and Systems Laboratory  
Chalmers University of Technology  
SE-412 96 Gothenburg  
Telephone +46 31 772 1000

Cover: Electrical discharge occurring between a molybdenum disulfide disk and a molybdenum rod.

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## Abstract

This project examines the possibility to produce material of two dimensions with the electrochemical method of spark erosion. Three transition metal dichalcogenides were examined, namely  $\text{MoS}_2$ ,  $\text{MoSe}_2$  and  $\text{WS}_2$ . Their layered crystal structure and semiconductor behavior make them interesting for nanoelectronic devices. The method of spark erosion could give a cost efficient and large scale production method. Spark erosion has previously shown to be a very effective method to exfoliate nanoparticles. This project investigates the possibility to reduce the dimensions of the produced material and create 2D nanoflakes.

The project includes a thorough description of the experiments conducted. Many different fields and methods were examined in order to find reliable results and conclusions. It includes electrophysics and electrochemistry, as well as nanosize characterization. The setup used to support spark erosion have been adjusted and altered to support the production of 2D materials, but it has not been optimized. It was possible to produce microparticles of  $\text{WS}_2$  but no single layer material was observed. A challenge was to separate the particles from the dielectric liquid of the setup, namely oleic acid. Centrifugation and chemical cleaning was used. To further examine the 2D material production with spark erosion the current and voltage of the setup needs to be tuned more precisely. This will effect the energy which is used to exfoliate the material.

Keywords: spark erosion, 2D material, arc discharge,  $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WS}_2$ , oleic acid



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# 1

## Introduction

Since a new method of producing single layer graphite, i.e. graphene, was discovered in 2004 [1], the research around graphene and other two-dimensional (2D) materials has grown rapidly. This is because of the interesting properties that come with the decrease of dimensions. Electrical, thermal and mechanical properties change and 2D materials gives the possibility to significantly decrease the size of electronic devices [2]. The special properties of graphene have led to extensive research on its fabrication methods and applications. Chalmers University of Technology has been part of the Graphene Flagship and Chalmers has become a center of graphene and other 2D material research [3].

The large scale development of graphene has left other 2D material behind. Some properties of graphene have some drawbacks and therefore the development of other 2D materials has to be investigated on a larger scale. One disadvantage of graphene is that it does not have a band gap, meaning that the conductivity can not be switched off, which is necessary in devices like transistors [4]. Instead, semiconducting 2D materials could be used.

Transition metal dichalcogenides (TMDCs) are semiconductors with layered crystal structure, which makes them interesting for applications of nanosized transistors and other switching electronics [5]. One crystal layer of these materials corresponds to the 2D nanoflakes required for these applications.

### 1.1 Aim

The aim of this project is to find a method to produce 2D materials on a large scale. The method examined is based on the established concept of electrical discharge machining [6]. It is well developed in cutting and shaping materials and also in micro and nanoparticle production, so called spark erosion [7], but not in single layer semiconductor production. The product of spark erosion is nanoparticles dispersed in a dielectric liquid. The particles are exfoliated from two electrodes, submerged in the liquid. Applying current and voltage over the electrodes induces a discharge between them, which break loose nanosized material from the electrodes. This material is dispersed in the liquid as particles and the aim is that they will be 2D nanoflakes.

The original hypothesis is that materials with layered crystal structure will be exfoliated layer by layer by the energy of the discharge in the spark erosion process.

### 1.2 Question formulation

In this project it has been investigated if it is possible to produce 2D nanoflakes that could be used for nanoelectronic applications. Being able to use them for these purposes, the 2D materials have to fulfill some requirements. First of all they need to be nanosized: mono- or few-layered. They need to be clean and should not have reacted with any of the chemicals involved in the production process. Good quality with minimal amounts of defects is also a requirement.

To produce semiconductor particles with spark erosion, especially 2D layered semiconductor particles, requires other electrical environments compared to produce metal nanoparticles. This has to be studied and optimized. Important parameters to study are the current and voltage applied and what dielectric liquid to use.

The three TMDCs examined in this report are molybdenum disulfide,  $\text{MoS}_2$ , molybdenum diselenide,  $\text{MoSe}_2$  and tungsten disulfide,  $\text{WS}_2$ . The difference of these materials was examined with respect on 2D material production.

# 2

## Theory

To fully evaluate the results of this project, a theoretical background is described here. The basic properties of 2D semiconductors and transition metal dichalcogenides give an insight in the wanted properties and what production methods that have been used previously to produce 2D nanoflakes for electronic applications.

Theory about spark erosion machines is presented, with the different components and the physics behind it. Additionally the section includes a short review of previous applications and the possibilities spark erosion has to produce 2D nanoflakes of MoS<sub>2</sub>, MoSe<sub>2</sub> and WS<sub>2</sub>. Electrochemical machining will also be described since it became a sidetrack of this project. The different characterization methods are presented in section 2.5.

### 2.1 Semiconductors and 2D materials

Semiconductors are materials defined by their small band gaps [8]. This makes it possible to tune their conductivity very precisely. By applying a voltage over the material the Fermi level will change, i.e. the highest energy level occupied with electrons. By applying positive or negative voltage the transport of electrons will be modified.

This makes semiconductors very applicable in switching electronic devices, such as transistors. Transistors are three terminal devices and the gate voltage of the device signal the transistor to be either conducting or insulating. There exists several different types of transistors and they are all relying on the properties of different semiconductor materials.

Moore's law describes how transistors grow smaller and smaller each year by advancement of technology [9]. This means that the transistors of today is advancing against nanosize, utilizing two dimensional material. Two dimensional meaning that the material is only one unit cell thick in  $z$ -direction, while it is an extended crystal in  $x$ - and  $y$ -directions [2]. Materials structured this way can be obtained from layered crystal structured materials.

## 2.2 Transition metal dichalcogenides

Transition metal dichalcogenides are materials that have the chemical formula  $\text{MX}_2$ , where M is a transition metal and X is a chalcogen, from group 16 in the periodic table [10]. They have layered crystal structure meaning that the atoms bond strongly to each other by covalent bond in one plane, giving one layer. The next layer of atoms are bonded to the first by the weaker van der Waals bond. The structure is visualized in Figure 2.1 [11].

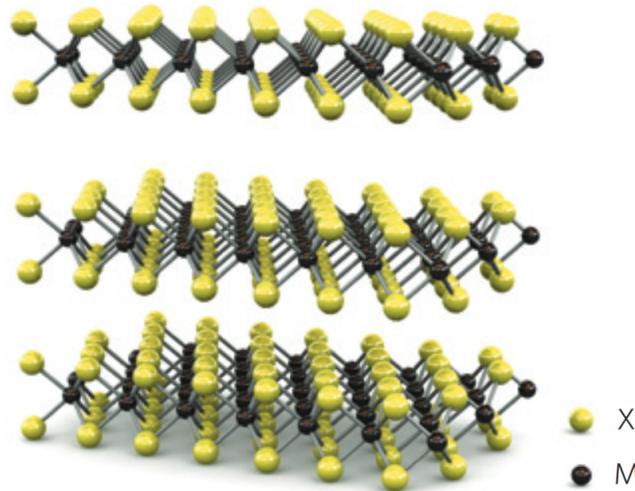


FIGURE 2.1: The crystal structure of TMDCs. Covalent bonds are shown as lines between the atoms.

[11]

The layered structure makes it possible to exfoliate TMDCs into 2D layers, which later could be used in nanodevice fabrication [12]. A monolayer semiconductor has different properties from those of a bulk semiconductor. For some materials the monolayer obtains a direct band gap instead of an indirect one.

In table 2.1 the melting point, the density and the electrical conductivity under different conditions are presented for each examined TMCD,  $\text{MoS}_2$ ,  $\text{MoSe}_2$  and  $\text{WS}_2$ . Conductivity and resistivity are related to each other according to  $\sigma = 1/\rho$ , where  $\sigma$  is the conductivity and  $\rho$  is resistivity. Their respective unit is siemens per meter ( $S/m$ ) and ohms times meter ( $\Omega m$ ) where  $S = 1/\Omega$ . It has been widely investigated how the electrical conductivity is affected by exfoliated-restacked TMDCs and concluded that these materials have lower conductivity than the pristine crystals [13].

TABLE 2.1: Melting point, density and conductivity of the three examined TMDCs. The condition under which the conductivity is measured is stated in the column to the right in the conductivity-table.

	MoS <sub>2</sub>	MoSe <sub>2</sub>	WS <sub>2</sub>	
Melting point	1185°C [14]	1200°C [15]	1250°C [16]	
Density	5.06 g/cm <sup>3</sup> [15]	6.9 g/cm <sup>3</sup> [15]	7.5 g/cm <sup>3</sup> [16]	
	MoS <sub>2</sub>	MoSe <sub>2</sub>	WS <sub>2</sub>	Conditions
Conductivity <i>S/cm</i>	0.03	0.2		Measured on rectangular samples prepared from respective element, an investigation of the temperature dependence. Room temperature conductivity [17].
Conductivity <i>S/cm</i>			4-7	Exfoliated-restacked WS <sub>2</sub> , lithium intercalation exfoliation and restacked into 1T-WS <sub>2</sub> . Room temperature conductivity [18].
Conductivity <i>S/cm</i>		p 0.007 e-r 0.05	p 0.5 e-r 0.04	Lithium intercalation exfoliation and restacked. p indicate pristine sample, e-r indicate exfoliated-restacked sample. Room temperature [13].
Conductivity <i>S/cm</i>	0.2-5.1			Samples of natural origin of MoS <sub>2</sub> . Measured on rectangular samples. Some samples were heat treated. Room temperature conductivity [19].
Conductivity <i>S/cm</i>	2.56	0.104	3.52	Average of the obtained values from the different articles studied.

Monolayers of TMDCs can be extracted using the scotch tape method or lithium based intercalation [2]. Also chemical exfoliation and other types of intercalation have been examined, the later has been used since the 1960s for production of few layered van der Waal materials [20]. The reason for this project is to scale up the production of 2D materials. With this new method of spark erosion a large amount of the materials could be produced and used in nanodevice fabrication.

### 2.3 Spark erosion

Spark erosion uses a similar setup as electrical discharge machining (EDM). In EDM and spark erosion, two electrodes connected to a power source are submerged in a dielectric liquid. When an electrical field is applied over the electrodes from the power source, it causes an electrical breakdown of the liquid. This means that a plasma channel is formed between the two electrodes which allows electrons to rapidly flow from the cathode to the anode.

In EDM this flow of electrons is used for cutting and shaping conducting materials. The anode, called workpiece, is shaped by the cathode, called tool. The high power of the breakdown melts or sublimates an area of the workpiece and removes materials from it to model it into desired shapes [6].

In EDM the product of the process is the anode. In spark erosion it is instead the dielectric liquid, and the dispersed material in it, distributed as particles. The process is approximately the same. The dielectric liquid surrounds the two electrodes and gathers the particles that are exfoliated from the anode. At each electrical breakdown, the high power plasma hits the target and melts or sublimates parts of it. The liquid then cools these droplets and bubbles and freezes or condensates and freezes them back to solids. The particles are then dispersed in the liquid.

The setup is demonstrated in figure 2.2. To the left the big circuit is shown and in the scale up to the right the plasma channel with surrounding evaporated liquid is shown between the electrodes. The shadowed area of the electrodes is the part which becomes partly exfoliated into the dielectric liquid.

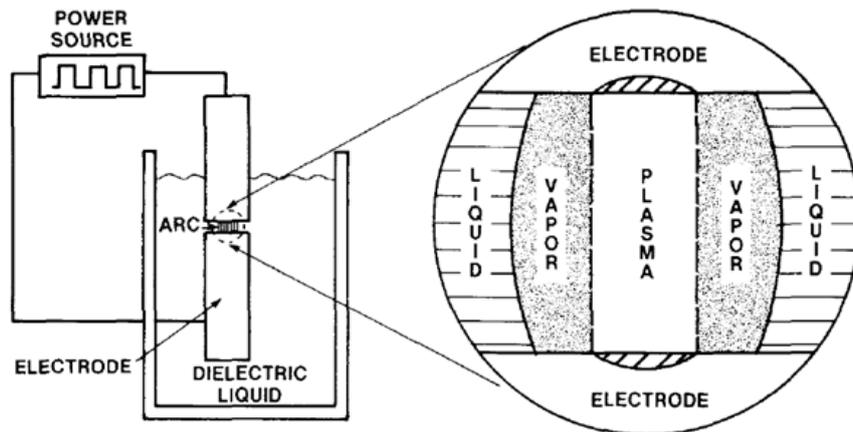


FIGURE 2.2: The spark erosion setup. On the left side is a full drawing of the setup and to the right is an magnification of the discharge region.

[7]

In spark erosion the anode is consumed to a larger extent than the cathode. During the breakdown electrons flow in the gap between the electrodes and ionize the liquid creating ions and more electrons. The ions are then accelerated to the cathode and the electrons to the anode. Due to the higher mobility of electrons than ions, short sparks favour anode wear. This results in consumed anode and a cathode barely affected [7].

To have an effective process the liquid should be circulated because particles in the gap reduce the spark strength. The particles disturbs the discharge between the electrodes and it can not reach full power.

Another important parameter is the dielectric liquid. The liquid should not be conducting, nor reactive and easy to separate from the produced particles. This because if the liquid is too conducting, electrical breakdown is hard to achieve. If the liquid can transport electrons, no breakdown is needed for completing the circuit. If the liquid is too reactive, it could react with the particles, the electrodes or the beaker which contains it. Easy separation is needed in order to be able to use the particles for different applications after exfoliation.

Deionized water is a commonly used liquid. With high current and low voltage applied from the power source, a spark is formed between the electrodes if the gap is small enough. There is a dependence between the gap size and the voltage applied, the bigger the gap is the more voltage is required to induce a spark, according to equation 2.2.

Metals and semiconductors exfoliates during different conditions in order to be exfoliated in a spark erosion process. Exfoliating metals do not require high voltage. Only applying a high current to the circuit makes the sparks powerful but the distance between the electrodes needs to be very small to compensate for the low voltage.

To exfoliate semiconductors with spark erosion higher voltages need to be applied. This is done in order to raise the Fermi level of the material in order to make them conducting. See the conductivity of the three TMDC materials in table 2.1. A too low voltage means that the electrons do not flow as easily, meaning that a discharge will not be ignited at all.

Simplified, the energy of each discharge is given by

$$E_s = Pt_s \quad (2.1)$$

where  $t_s$  is the time duration of the spark, usually around  $1 \mu s$ , and  $P$  is the power of the discharge described by

$$P = VI \quad V = IR \quad R = \rho d \quad (2.2)$$

according to Ohm's law.  $V$  is the voltage,  $I$  is the current,  $R$  is the resistance of the electrode gap,  $\rho$  is resistivity of the dielectric liquid and  $d$  is the distance between the electrodes. The spark erosion is therefore dependent on the current and the voltage from the power supplier and also the resistivity of the dielectric and the distance between the electrodes. Higher voltage and lower current means that the resistance of the dielectric needs to be higher for a discharge to occur, otherwise the dielectric will become electrically conductive. If the resistance remains the same, a higher voltage will allow electrons to flow between the electrodes.

For comparison the resistivity and the breakdown voltage of air and water is presented. For air the resistivity is  $3 \cdot 10^{14} \Omega\text{m}$  and the breakdown voltage is 3 kV/mm [21]. For water the respective numbers are  $1.5 \cdot 10^5 \Omega\text{m}$  and 60 kV/mm [22]. High current and low voltage can induce a discharge in both medium, low current and high voltage can only induce it in air, since the water becomes conducting.

The mass loss of the electrodes has been described by Pfeiffer T. *et.al.* [23]. An energy balance can be derived under the assumption that a percentage of the spark energy, given by  $\alpha$ , does not contribute to the evaporation of the electrodes. This energy is instead radiated and conducted to the surrounding dielectric liquid. The energy balance is given by

$$\begin{aligned} \alpha E_s - \pi r^2 \sigma t_s T_{boil}^4 - 2\pi r t_s k (T_{boil} - T) = \\ m c_{ps} (T_{melt} - T) + m c_{pl} (T_{boil} - T_{melt}) + m H_{melt} + m H_{vap} \end{aligned} \quad (2.3)$$

where  $r$  is the radius of the spark or the area affected on the electrodes.  $\sigma$  is the Stefan Boltzmann constant, approximated to the value of a black body.  $T_{boil}$  is the boiling point of the electrode,  $T_{melt}$  is the melting point and  $T$  is the room temperature.  $k$  is the heat conductivity of the electrodes and  $m$  is the mass consumed of the electrodes.  $c_{ps}$  and  $c_{pl}$  are the heat capacity for solid phase and liquid phase respectively and  $H_{melt}$  and  $H_{vap}$  are the enthalpy of melting and evaporation respectively. The first term to the left of the equality sign is the energy from the spark contributing to the erosion. The following term is the heat radiation from the electrodes and the next term is heat conduction in the electrodes from the heated area. The first term right of the equality sign is the energy it takes to heat the material to the melting point. The following term is the energy it takes to heat it to the boiling point. The two last terms are the energy it takes to melt and evaporate the material respectively. Everything to the right of the equality sign equals the enthalpy of sublimation,  $\Delta H_{sub}$ , times the mass.

### 2.3.1 Dielectric

To fully evaluate the spark erosion process the theory behind permittivity and dielectric materials needs to be covered.

Permittivity,  $\epsilon$ , measures a mediums ability to decrease the electric field,  $\mathbf{E}$ , between two charged areas. Its unit is F/m or C/(Vm). The higher permittivity, the lower electric field and the lower resistivity of the medium. The permittivity of materials is normally denoted relative to that of vacuum,  $\epsilon_0$ , which has the value of  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$  and is defined as  $\epsilon_0 = 1/(\mu_0 c^2)$ , where  $\mu_0$  is the permeability of vacuum and  $c$  is the speed of light. The relation is described by

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (2.4)$$

where  $\epsilon_r$  is the relative permittivity. This variable is often denoted as the dielectric constant,  $\kappa$  ( $\kappa = \epsilon_r$ ). A dielectric liquid is an insulating medium that gets polarized by an applied electric field. The polarization makes the medium more conducting.

The higher polarization the higher permittivity of the medium. The polarization is time dependent and described by

$$\mathbf{P}(t) = \epsilon_0 \int_{-\infty}^{\infty} \chi(t-t') \mathbf{E}(t') dt' \quad (2.5)$$

where  $\chi$  is the time dependent susceptibility and  $\chi(\Delta t) = 0$  if  $\Delta t < 0$ .  $\epsilon_r$  could therefore also be described as  $\epsilon_r = 1 - \chi$ . Equation 2.5 could be Fourier transformed with respect to time and instead become a equation of frequency,  $\omega$

$$\mathbf{P}(\omega) = \epsilon_0 \chi(\omega) \mathbf{E}(\omega) \quad (2.6)$$

which makes the polarization as a simple equation of addition [24].  $\epsilon_r$  is now dependent on the frequency and the value is often specified at the frequency 1 kHz.

The dielectric liquid used for spark erosion span many different liquids [25] [26] [7] [27]. The most commonly used is deionized water. It provides a nonreactive solvent and is easily separated from the produced particles by evaporation. Metals and metal alloys are the most common material exfoliated in water. For very reactive materials liquid argon or liquid nitrogen can be used [26]. Other possible liquids are organic solvents, silicon oil and kerosene [25]. Dodecane has also been used, but then the use of surfactant is necessary in order to keep the produced particles from recombining [7]. The dielectric constant of some interesting liquids is presented in table 2.2.

TABLE 2.2: Dielectric constants of different liquids.

	Air	Water	Dodecane	Oleic acid	Chloroform	Nitrogen(l)
Dielectric constant	1 [28]	80 [29]	2.01 [30]	2.5 [29]	4.8 [29]	1.55 [31]

## 2.4 Electrochemical machining

Electrochemical machining is a type of exfoliation process where electrically conducting materials can be shaped and modified. Its physics is based in the electrochemical principle of electrolysis. An anode, so called workpiece, and a cathode, so called tool, are submerged in a conducting liquid. An electric potential is applied over the two electrodes which make current flow from the anode, through the liquid to the cathode. At the cathode hydrogen gas is evolved which does not effect this electrode, meaning that the tool is unaffected throughout the process. At the anode, on the other hand, the process dissolve the material.

The process has been mathematically investigated for a metal workpiece in Bhattacharyya B. *et al.* [32]. The material removal rate is described by

$$r \propto \frac{J\eta}{\nu F \rho} \quad (2.7)$$

where  $J$  is the current density,  $\eta$  is the metal dissolution efficiency,  $\nu$  is the valence of metal dissolution,  $F$  is Faraday's constant, and  $\rho$  is the density of the metal. The removal rate is mainly dependent on three different factors:

- Reactions at the anode and current efficiency which describes the dissolution efficiency,  $\eta$ . Different combinations of workpiece and electrolyte compounds contribute differently to the removal rate.
- Mass transport effects which give an optimal current density,  $J$ . The higher the current density the more particles are produced. But if they do not have the time to diffuse away from the anode, they create a protective layer which prevent further exfoliation. The optimum is therefore between current density and mass diffusion in the liquid.
- Current distribution and shape evolution which effect the current density,  $J$ . The machining will effect the shape of the anode and the distance between the electrodes. The current distribution at the anode depends on the geometry, kinetics of the anode reactions, electrolyte conductivity and hydrodynamic conditions.

## 2.5 Characterization methods

### 2.5.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a imaging tool which utilizes an electron beam to image a surface and gives a high resolution picture. The beam scan the surface and the electrons interact with the material. This causes signals like auger electrons, secondary electrons and X-rays that are detected as they scatter from the surface and result in the image. The electrons only give a clear picture over conducting materials. If an insulator is scanned it will result in charge effects which make it difficult to focus and to get a good contrast. Insulating materials can be coated by a metal layer in order to get a good picture. The reason the resolution of a SEM is higher than for a optical microscope is that the wavelength of electrons is smaller than for photons. They can therefore detect smaller changes of the surface compared to an optical microscope [33].

### 2.5.2 Transmission electron microscopy

Transmission electron microscopy (TEM) also utilizes an electron beam to image samples. Instead of detecting the signals scattered back from the sample as in SEM, TEM detects the electrons that are transmitted through the sample. The sample has to be thin enough for electron to be transmitted through in order to get a good image [34].

### 2.5.3 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) is used to map the elements present in a sample. It detects the X-ray emission from the sample as it interacts with an

electron beam. Each element has its own specific X-ray emission which makes it possible to distinguish different elements. The read-out of an EDX is a diagram with the number of counts of each element against the elements and their different energies of the X-ray signal. The data given from EDX is not very reliable since it generates a lot of noise and could give weak signals of some elements [35].

#### **2.5.4 Raman spectroscopy**

Raman spectroscopy utilizes photon-phonon interaction of materials. A laser beam is aimed at the sample which will be investigated. The light then interacts with the vibrational modes of the molecules of the sample. These different modes gives different scatterings of the light. The scattered light is then detected and analyzed by the software and this tells what molecules are present. It is visualized in diagrams where the shift of the light, due to the phonon interaction, is shown as peaks. In Raman spectroscopy it can be distinguished if the material is single layer, few layered or bulk and is therefore a good characterization method for 2D materials [36].



# 3

## Methods and results

In this chapter the project will be described chronologically. Since the aim of this project is to investigate if 2D flakes of the semiconductors can be produced using spark erosion, each step in this process and the respective results are presented in order to follow the projects process.

### 3.1 Preparation of materials

The starting material of each compound was powders bought from Sigma-Aldrich with purity of  $\text{MoS}_2$  99%,  $\text{MoSe}_2$  99.9% and  $\text{WS}_2$  99%. To produce bulk materials of these, they were first pressed and then annealed into disks. This was made in a cylinder where the powder was processed between two protective blocks with a rod. The inner diameter of the cylinder, and thus the diameter of the disks, was 13 mm. For pressing, a hydraulic press was used where maximum 15 tons of weight could be applied. For annealing, a high temperature furnace was used with maximum temperature of  $650^\circ\text{C}$ .

Different times, pressures and temperatures were examined. For  $\text{MoSe}_2$  pressing with 8 tons for two hours and then annealing in  $400^\circ\text{C}$  for two hours was sufficient for a compact and non porous disk. For  $\text{MoS}_2$  and  $\text{WS}_2$  it was harder to obtain disks of proper quality. The highest temperature provided from the furnace for more than two hours was  $450^\circ\text{C}$ . This low temperature resulted in that they got split up, instead of being one thicker disk. In figure 3.1 the obtained disks are shown after some use.



FIGURE 3.1: The disks produced for the spark erosion experiments. The materials are from right to left:  $\text{MoSe}_2$ ,  $\text{MoS}_2$  and  $\text{WS}_2$ .

The MoS<sub>2</sub> disks were produced by pressing of 12 tons for one and a half hour and annealing in 450°C for three hours. The WS<sub>2</sub> disks were produced with pressing of 12 tons for two hours and annealing in 400°C for two and a half hour.

The density of the disks was measured to secure that the disks could be considered bulk material and not be too porous. The final disks, used for the experiments described in section 3.4, had the following densities: MoSe<sub>2</sub> 4.7 g/cm<sup>3</sup>, MoS<sub>2</sub> 5.7 g/cm<sup>3</sup> and WS<sub>2</sub> 6.9 g/cm<sup>3</sup>. In comparison with the values of table 2.1 these are dense enough for the performed experiments.

## 3.2 Original spark erosion machine

The original setup of the spark erosion machine had the same schematic as shown in figure 2.2. The original power supplier was a high current welding machine that could assist with currents up to approximately 170 ampere and voltages of about 28 volts. The setup has previously been used for metals, mainly copper and iron, using deionized (DI) water as dielectric. This machine was provided by the company SHT Smart High Tech AB [37]. The machine works with approaching an arm with the anode towards the cathode. When a discharge occurs, the anode is withdrawn and then set to approach again in order to quickly consume the material. This is repeated until a set distance of the anode is consumed.

### 3.2.1 Discharges in water

Initially the original setup of the spark erosion machine was used. The cathode rod for the MoS<sub>2</sub> and MoSe<sub>2</sub> disk experiments was made out of molybdenum, Mo. For WS<sub>2</sub> the cathode rod was made out of tungsten, W. The reason for this was to reduce contamination as much as possible, only having the relevant elements present in the experiments.

The initial experiment is shown in figure 3.2. The MoS<sub>2</sub> disk is held by an iron clamp and approaches the Mo rod with DI water as dielectric. Spark erosion for this setup did not occur. The picture to the right shows how the disk crashes into the rod as no breakdown was initiated. The crash also implies that no current ran through the circuit even as the disk touches the rod. If the circuit would have been shorted by the contact of anode and cathode, the arm would pull back up again as instructed by the software.



FIGURE 3.2: The original setup of the spark erosion machine.

This means that the low voltage applied to the circuit is not enough to make the semiconductor material of the disk conducting. Even in direct contact between the anode and the cathode, current is not flowing. This means that the  $\text{MoS}_2$  disk behaves like an insulator.

### 3.2.2 Electrochemical machining

It became evident that a high voltage power supplier was required in order to increase the Fermi level of the semiconductors to the point where they became conducting. During the process of acquiring a high voltage supplier, the parameters of the dielectric liquid were changed in order to see if it was possible to obtain a spark with the high current supplier. An idea of making the dielectric more conducting was tested, which now is understood to be the wrong approach. A better conducting liquid does not contribute to a better electrical breakdown environment.

In the setup described in section 2.3, the use of ionized water was sufficient to initiate electrochemical machining. Sodium chloride,  $\text{NaCl}$ , was added to the deionized water to investigate if higher conductivity of the water could induce a spark. The opposite effect was obtained. By the increased conductivity of the water, current flow through the liquid and no electrical breakdown did occur, meaning that discharges could not happen. Instead, this caused electrolysis of the water. The anode got exfoliated by this process, described in section 2.4

It shows that this process was more effective to exfoliate metals than semiconductors. This is because the iron clamp that holds the investigated materials also was exfoliated when it touched the water and resulted in more exfoliated material than if only the semiconductor disk was submerged. Figure 3.3 shows how the clamp was affected by the electrochemical machining. Figure 3.4 shows a comparison between when only the disks are submerged and when both the disk and the clamp are submerged. When only the disk is submerged hydrogen bubbles are created and no difference in colour of the water is seen. In contrast, when the clamp is submerged the iron particles colour the water immediately, seen in the picture as darker stains.

### 3. Methods and results

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FIGURE 3.3: The vial to the left in the picture is sodium chloride water with exfoliated iron from the clamp. To the right is the clamp where the effect from the electrochemical machining is visible as an oxidized area.

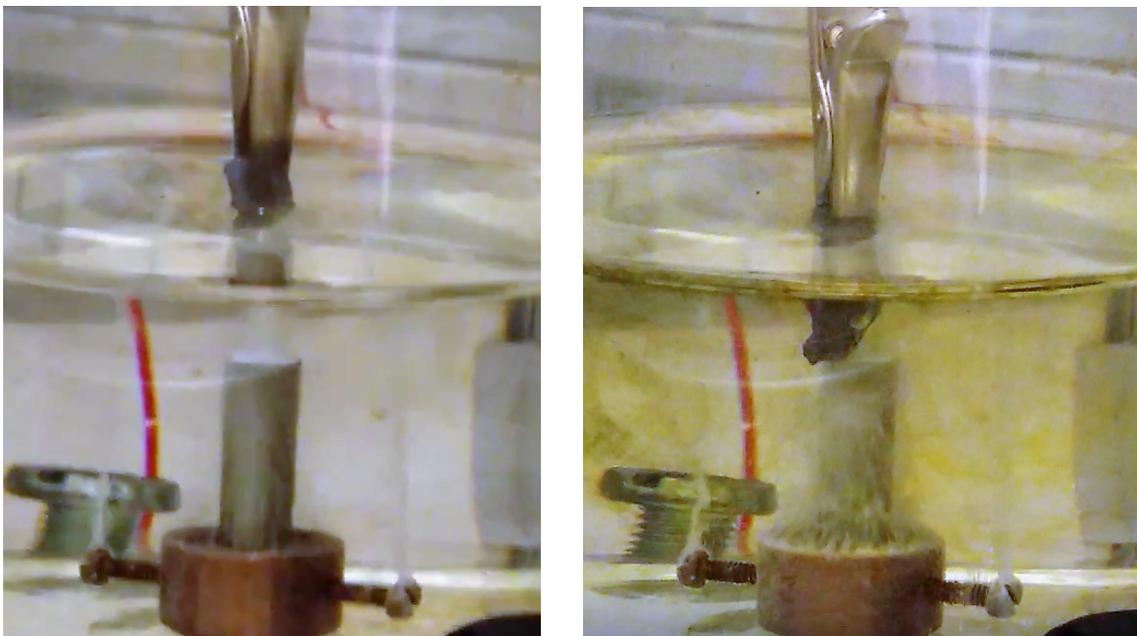
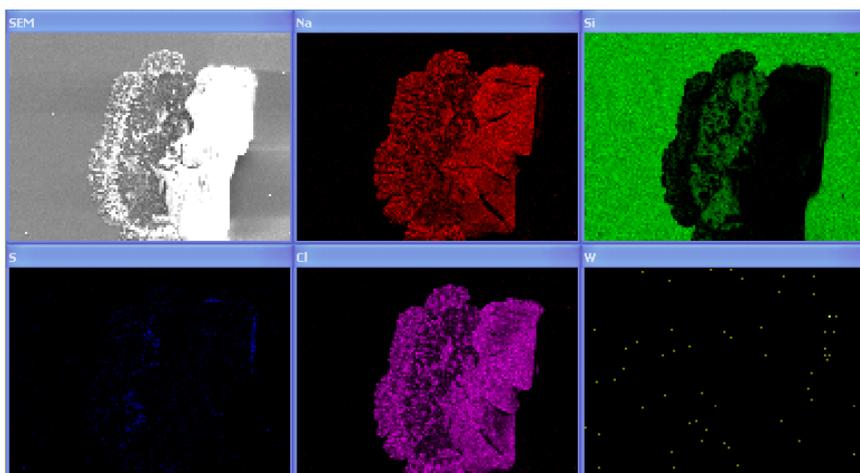


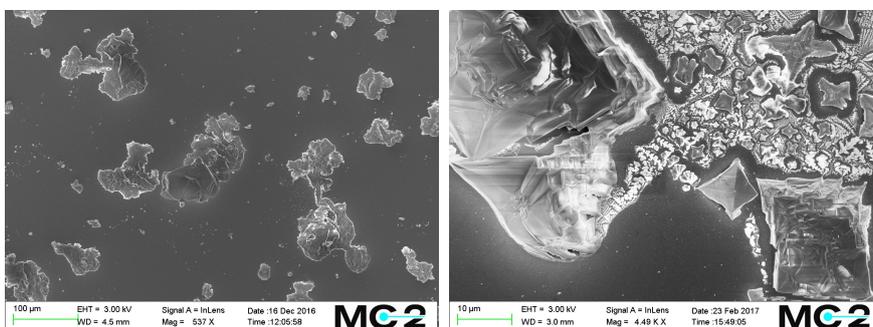
FIGURE 3.4: The left picture shows the case when only the semiconductor disk is submerged in water. The right picture is from the same experiment with also the clamp in the water. The bubbles are hydrogen gas produced at the cathode. The black-yellow dirt in the water of the right picture is exfoliated material from the clamp after just a few seconds in the water.

It was not possible to measure the consumed material via weighing the disk. This is because the material lost small pieces when just touched with tweezers or paper. The amount of exfoliated material from the process was very small compared with how much was scraped of from the disk in handling.

The produced solution from the electrochemical machining was characterized using SEM and EDX, described in section 2.5. The solution that was characterized was from when only the disk was submerged in the liquid, in order to not have iron contaminations. The solution was dripped on a silicon wafer for these characterizations. The obtained pictures are shown in figure 3.5. No particles from the semiconductors could be observed on these samples, only the sodium chloride crystals. In figure 3.5 A the elements of one of these particle are shown. Not much of the wanted material,  $WS_2$ , is present. Another indication that the particles are sodium chloride is that there were high charging effects in these areas. Since these salt crystals are not conducting, current crowding occurs when the electron beam in the microscope is aimed at them. This is shown as white, bright areas in the pictures.



(A) Mapping over the elements present in a particle seen in SEM, from a  $WS_2$  disk.



(B) SEM picture from  $MoS_2$  (c) SEM picture from  $WS_2$  sample.

FIGURE 3.5: Figure A, colour coding: red is Na, green is Si, blue is S, pink is Cl and yellow is W. In figure B and C two SEM pictures shows typical NaCl crystals.

## 3.3 High voltage spark erosion

The high voltage power supplier used for the remaining experiments could assist with voltages up to 10 kV and current of 2.5 mA. This supplier replaced the current supplier from the original setup and was connected to the electrodes. The higher voltage did make the semiconductor disks conducting. However, the increased voltage also caused the water to become conductive which prevents electrical breakdown of the liquid.

In figure 3.6 sparks are visible between the water surface and the disk. This means that the water is conducting enough to work as an electrode itself and the high voltage, around 6 kV, makes it possible for breakdown in this gap of about 2 mm of air. That the sparks occur here does unfortunately not give any measurable results. In order to collect the exfoliated material, the spark erosion has to occur in liquid. Otherwise the particles will not cool as quickly and might spread outside the system, which makes it hard to collect them.



FIGURE 3.6: Discharges between the water surface and a MoSe<sub>2</sub> disk with the high voltage power supplier.

### 3.3.1 Investigation of dielectric liquids

Since the water could not be used as a dielectric liquid with the high voltage supplier, another liquid had to be used for the discharge to occur. The main property that had to be changed was conductivity of the liquid when exposed to high voltage. The medium also had to match the following conditions:

- Low dielectric constant, because of the hypothesis that it will reduce the electrical conductivity when the voltage is applied. For relevant dielectric constants, see table 2.2.
- Non flammable. A flammable liquid could be ignited by the high energy density of the discharge.
- Liquid in room temperature. The setup used in this project did not support any cooling or heating of the liquid.

- Non hazardous. In the setup one is bound to work close to the beaker containing the liquid meaning that hazardous vapor or similar should not be handled.
- High thermal conductivity. This will contribute with faster cooling of the exfoliated particles.

### 3.3.2 Discharges in oil and oleic acid

At first, a trial with Milli-Q water was made. This is described as ultra-pure water with the amount of ions in it minimized. This did not work, the water was still too conducting and no spark could be induced.

The next liquid tested was oil. Because its availability, rapeseed oil was bought and used for the initial tests. Replacing DI water with rapeseed oil did work, sparks could now be ignited in the gap between the electrodes when immersed into the oil. In figure 3.7, the left picture show a small spark in the gap as a white spot. This spark has very low energy compared to the discharges happening with the high current power supplier, shown in the right picture of figure 3.7. This because the spark now has lower current contribution, but higher voltage contribution.

Even if the spark actually occurs here it is uncertain if it will exfoliate any material. The yellow colour of the oil makes it hard to see if there is any colour change of the liquid. The very small spark implies that not as much material will be consumed as in the more powerful discharges of the original setup. Even though the disk may actually be consumed it is not certain that it is nanoflakes that will be produced.

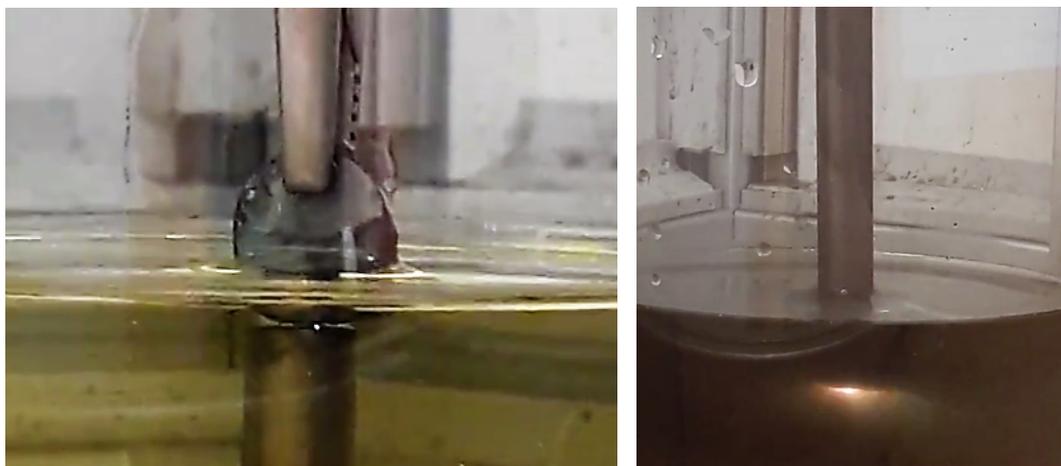


FIGURE 3.7: The discharge could be induced in rapeseed oil and is here shown as a small dot of light in the gap between the electrodes in the figure to the left. To the right a discharge is shown for iron in DI water with the high current supplier. The difference in the spark energy is clear. The water of this picture is dark because of the dispersed material in it.

#### 3.3.2.1 Separation from oil

In order to characterize the particles they had to be separated from the oil. The established method to do this with the original setup of the spark erosion machine was by centrifugation. In order to fully separate the particles the centrifugation had to be complemented with the use of other chemicals.

To dilute the oil with isopropanol,  $C_3H_7OH$ , with one part oil against more than four parts isopropanol, results in an one phase solution. For example: mixing water and oil this way would result in a two phase solution. The particles are likely to have some fatty acids from the oil bound to their surfaces, which make them hydrophobic. In a centrifugation process this would result in that the particles stayed in the oil phase instead of being centrifuged down to the bottom of the centrifuge tube.

When isopropanol instead is added the entire solution is hydrophobic which makes it possible for the particles to settle to the bottom. Discarding the supernatant after the centrifugation and adding more isopropanol removes more and more oil and washes the particles. To finally dissolve the fatty acids from the surface of the particles, a small amount of toluene,  $C_6H_5-CH_3$ , was added after all remaining supernatant was removed. This with the intention to dissolve the fatty acids and after drying and evaporation only leave the semiconductor particles.

The toluene solution was dripped on a gold wafer and left for drying. It turned out that not all the oil had been separated. In figure 3.11 the top two samples are the dried toluene solutions. The dry-marks shown are oil residues still left after the centrifugation process.

Putting these samples in the SEM resulted in the pictures in figure 3.8. Here the drying marks from the oil is shown as grey lines along the picture. In figure 3.8C one of the drying marks is shown as a very clear black border. The spiky crystals in A, B and D are believed to be a mix between the semiconductor elements and oil residues.

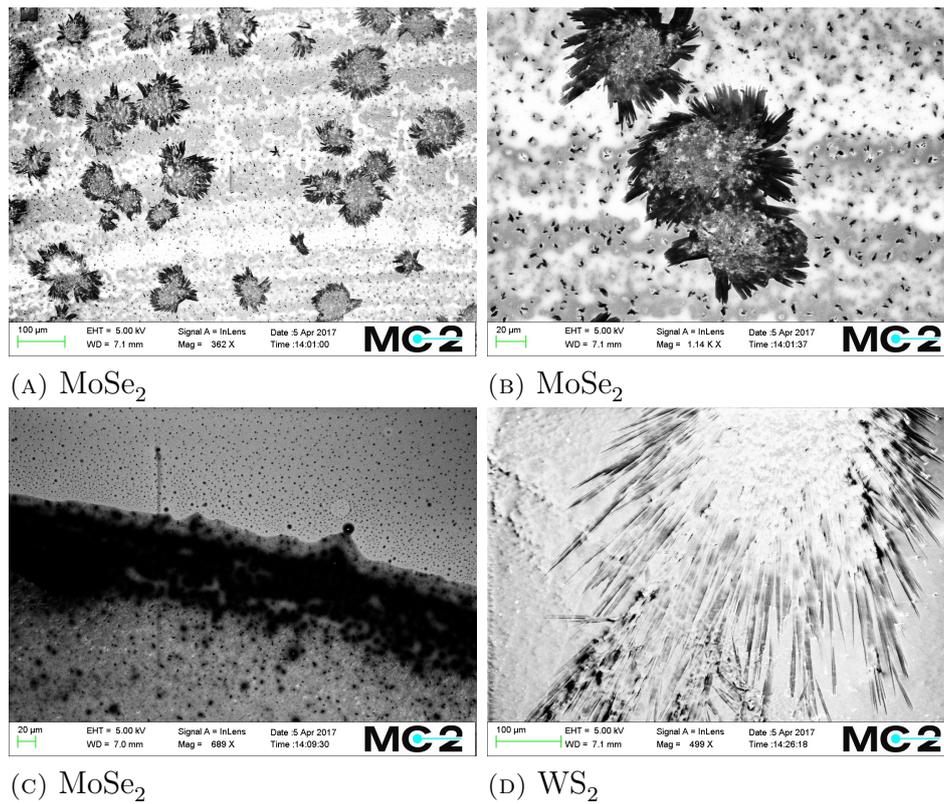


FIGURE 3.8: SEM pictures of some particles not fully separated from the oil. Pictures from the MoSe<sub>2</sub> and WS<sub>2</sub> samples.

The particles were examined in TEM, the pictures shown in figure 3.9. From these pictures the same conclusion can be drawn; the big particles are oil residues and the black spots in them might be small particles from the semiconductor material. The EDX measurements shown in figure 3.10 give a big count for copper and carbon, which probably are present from the TEM environment. It also give counts for the respective metals, molybdenum and tungsten, but very little for the chalcogenides, sulfur and selenium.

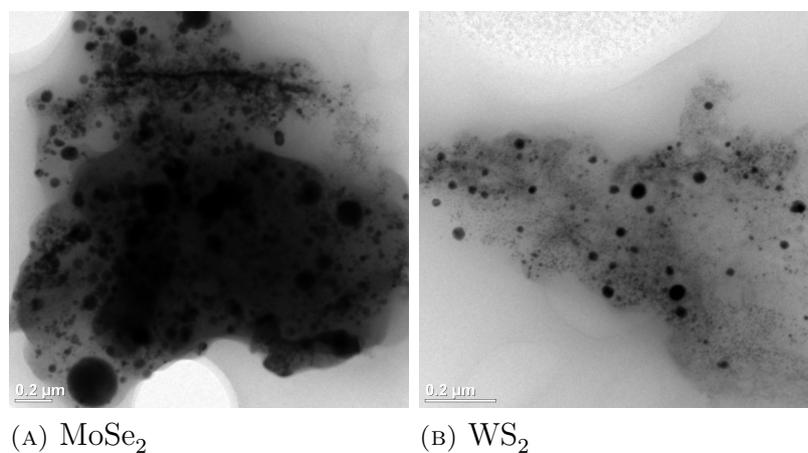


FIGURE 3.9: TEM pictures of some particles not fully separated from the oil. Pictures from the MoSe<sub>2</sub> and WS<sub>2</sub> samples.

### 3. Methods and results

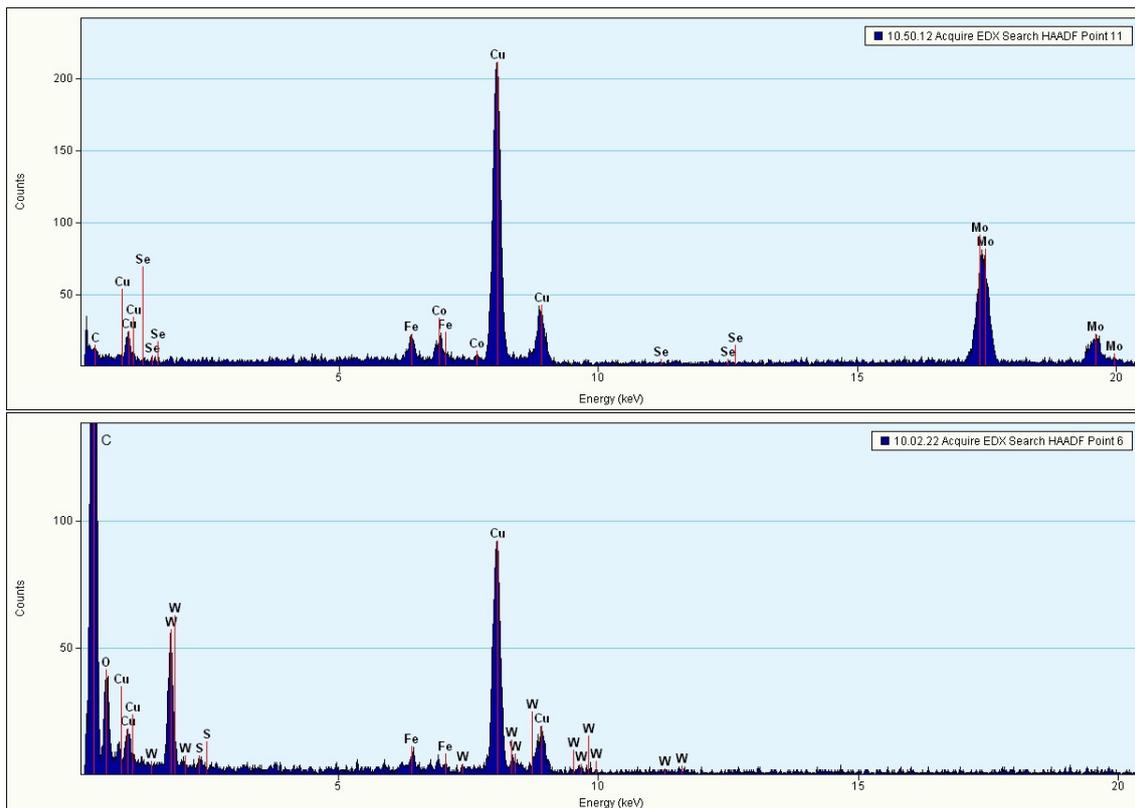


FIGURE 3.10: EDX for particles found in the TEM machine. The top diagram is from a  $\text{MoSe}_2$  sample and the bottom diagram is from a  $\text{WS}_2$  sample.

A trial with separating the oil via evaporating it, having boiling point higher than  $300^\circ\text{C}$ , failed because of the unclean composition of the oil. Instead it became a hard and darkened shell, also shown in figure 3.11 as the two bottom samples. This is fried oil, carbonized due to the oxygen in the air.

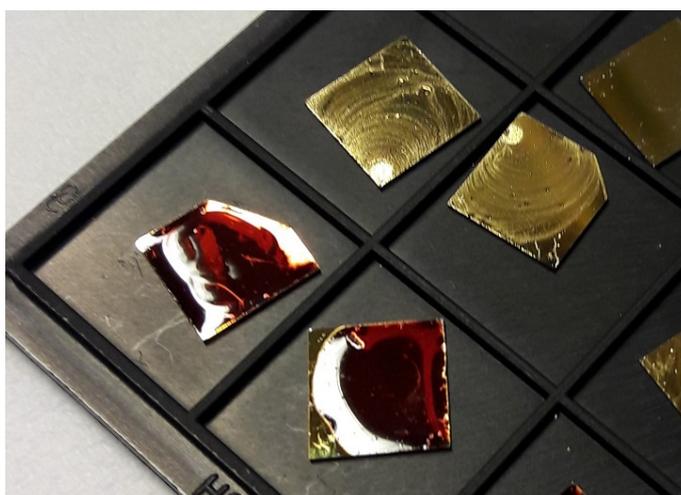


FIGURE 3.11: Samples where the particles were tried to be separated from the rapeseed oil by evaporation. The top two ones are  $\text{MoS}_2$  and  $\text{MoSe}_2$  from the toluene solution and the two bottom ones are dried and fried oil.

### 3.3.2.2 Properties of oleic acid

To get cleaner experiments and experiments with high reproducibility oleic acid was used for further examinations, the chemical composition and formula shown in figure 3.12. The purity of the oleic acid used in this project was 90%. This is one of the most common fatty acids of ordinary oil and the hypothesis was that it would work as the dielectric liquid with the high voltage power supplier. Oleic acid has a low dielectric constant, seen in table 2.2. After a first test with this liquid it was concluded that it does work for inducing discharges.

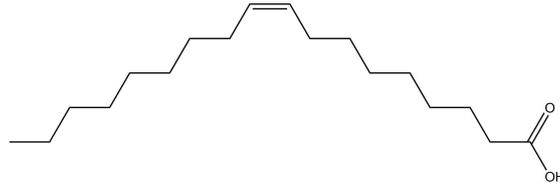


FIGURE 3.12: The chemical composition of oleic acid,  $C_{18}H_{34}O_2$

Using oleic acid can result in easier separation. This is because the rapeseed oil is not chemically clean and could therefore leave the residues shown in the characterizations. These residues contains not only oil but also aromas and other molecules. But the separation still includes centrifugation steps and washing of micro- and nanoparticles which is complicated.

### 3.3.3 Other dielectrics

During the examination of oleic acid as the dielectric a trial was made where polymers were dissolved into the DI water. Polymers are usually very apolar which could reduce the conductivity enough to be able to induce an electrical breakdown in water. Figure 3.13 shows a summary of the polymers investigated and the concentrations used. These polymers were tested because they were easily accessible and are relatively easily dissolved in water.

### 3. Methods and results

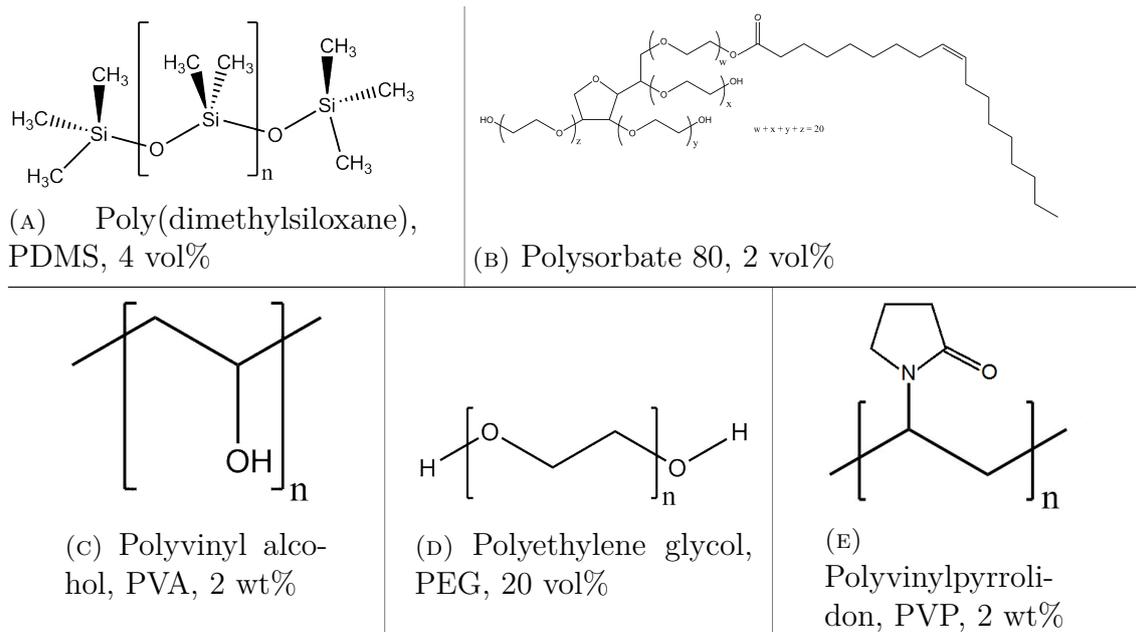


FIGURE 3.13: The different polymers dissolved in DI water in order to test if it increased resistivity of the water. The concentrations of the different polymers are presented in respective caption of the polymer.

Neither of these solutions can reduce the conductivity enough to induce a discharge. Other liquids were considered, for example organic solvents. Chloroform,  $\text{CHCl}_3$ , was one of them. It is very volatile, meaning separation of particles could be done easily, with evaporating the chloroform after the spark erosion process. But the low boiling point in combination with its carcinogenicity also makes it hazardous and it was concluded that it was too dangerous to use.

## 3.4 Functioning discharges in oleic acid

No other medium was found that could meet the criteria of this setup. Instead a more thorough investigation of the oleic acid was made, since this was the only clean liquid which could induce break down with the high voltage power supplier.

Even though discharges could be initiated for all three TMDCs in oleic acid, not all of them provided production of semiconductor particles. The only material which showed some reliable results was  $\text{WS}_2$ , where fragments of the disk had been consumed, see figure 3.14. Here the top of the disk is flattened and darker, changes caused by the spark erosion. The oleic acid also changed colour during the process, turning darker. This indicated that consumed material of the disk actually got dispersed into the liquid. Figure 3.15 shows a comparison between before and after spark erosion. The liquid is darker after the spark erosion, here preformed for one hour.

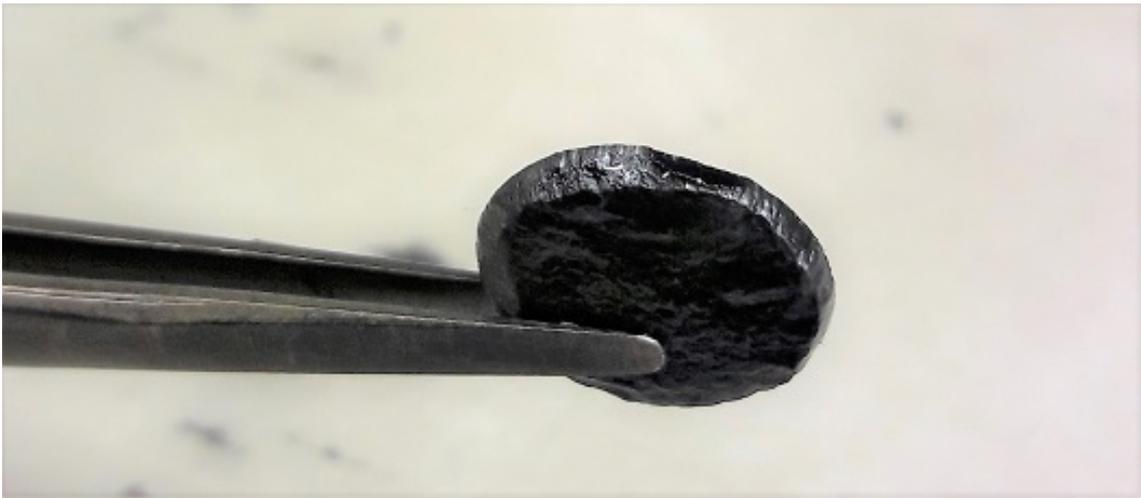
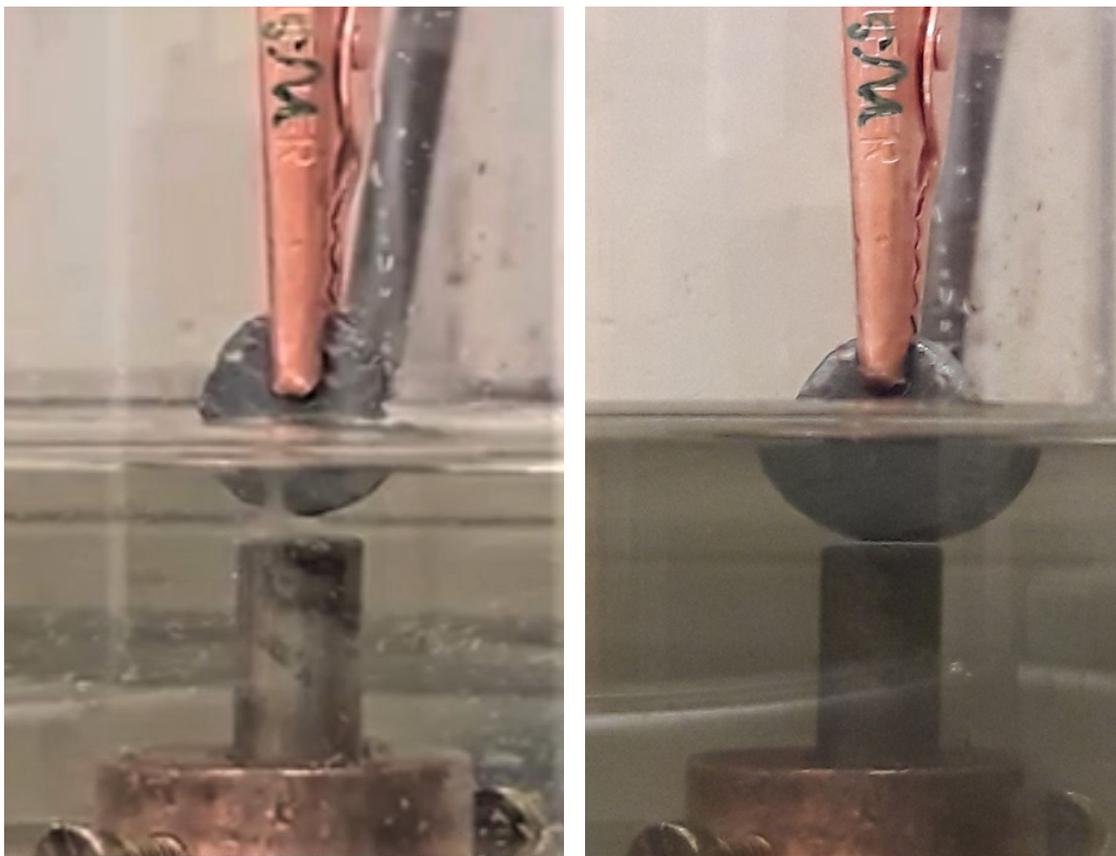


FIGURE 3.14: The  $WS_2$  disk got consumed during the spark erosion. The top of the disk is darkened and eroded.



(A) Before spark erosion.

(B) After spark erosion.

FIGURE 3.15: Figure A shows the colour of the oleic acid before the spark erosion and figure B after. The liquid is visibly brighter in A than in B.

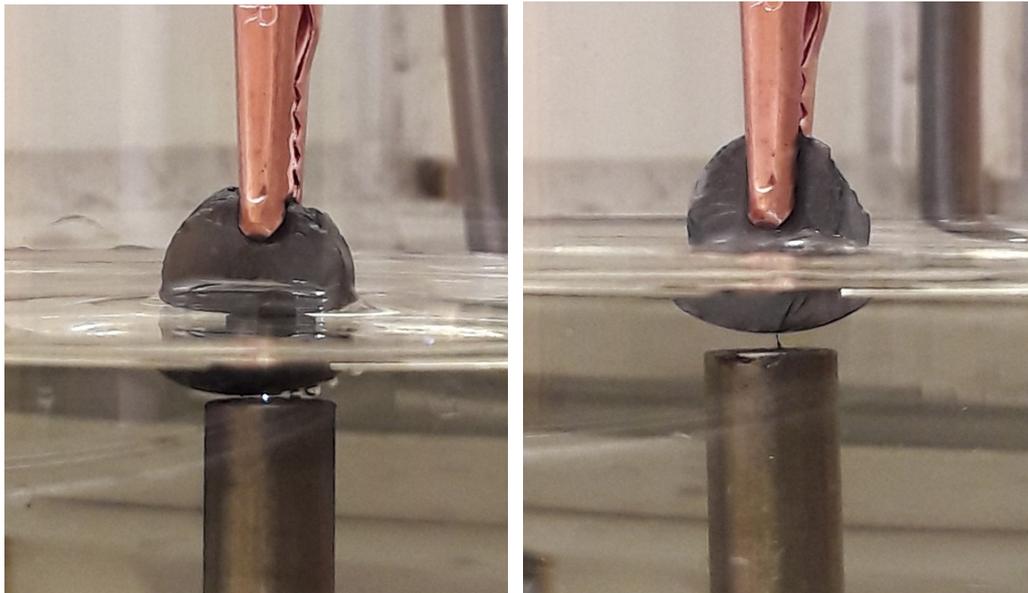
### 3. Methods and results

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The oleic acid kept its darker colour even after leaving it for a few days, forming a colloidal dispersion. This indicates that the particles dispersed in the liquid were very small, micro- or nanosized. If they would have been bigger they would have settled to the bottom during this time.

The two molybdenum based disks did not provide any particles even though discharges occurred, see figure 3.16. The difference can depend on the following factors:

- Enthalpy of sublimation,  $\Delta H_{sub}$ , of the materials. If the  $\Delta H_{sub}$  for the material is higher than the energy produced by the spark contributing to the sublimation, it will not exfoliate the material. See equation 2.3 for the mathematical description of this scenario.
- Conductivity of the semiconductors. Higher conductivity will probably give higher power of the discharge, since more current will contribute to it. The higher conductivity the more powerful discharges.  $WS_2$  has the highest conductivity of the materials investigated, as seen in table 2.1. 2.1.
- Porosity of the disks. If the disks are very porous their resistivity is higher which makes the discharges less powerful, as discussed in the factor above.



(A)  $MoSe_2$  disk

(B)  $MoS_2$  disk

FIGURE 3.16: Spark erosion of  $MoSe_2$  and  $MoS_2$ . In figure A there is a small constant spark between the electrodes. In figure B a small pillar of material has connected the electrodes and the circuit is shorted.

### 3.4.1 Different scenarios during the spark erosion

In figure 3.16 two typical scenarios during the spark erosion process are shown. To initiate the discharge the distance between the electrode has to be very small, with this voltage supplier around 0.3 mm. After the distance is adjusted the voltage is step-wise raised until a spark appears. Sometimes the spark flickers, sometimes it is constant. It has been mention by Pfeiffer T.V. *et.al.* that a constant spark does not contribute with enough energy to evaporate the material [23], since the energy will get lost by heat conduction through the electrodes, see equation 2.3. When the spark instead is flickering it could travel along the edge of the disk, see figure 3.17. It was hard to keep the spark erosion for a longer time. Bigger parts of the disk could fall off and connect the electrodes, making current flow without initiating any more discharges, see figure 3.16 B. When pulling the top electrode up a spark occurred and the power of it blew away the disturbing material. Lowering the electrode again and the spark could be initiated once more. A thorough description of the process is presented in appendix A.

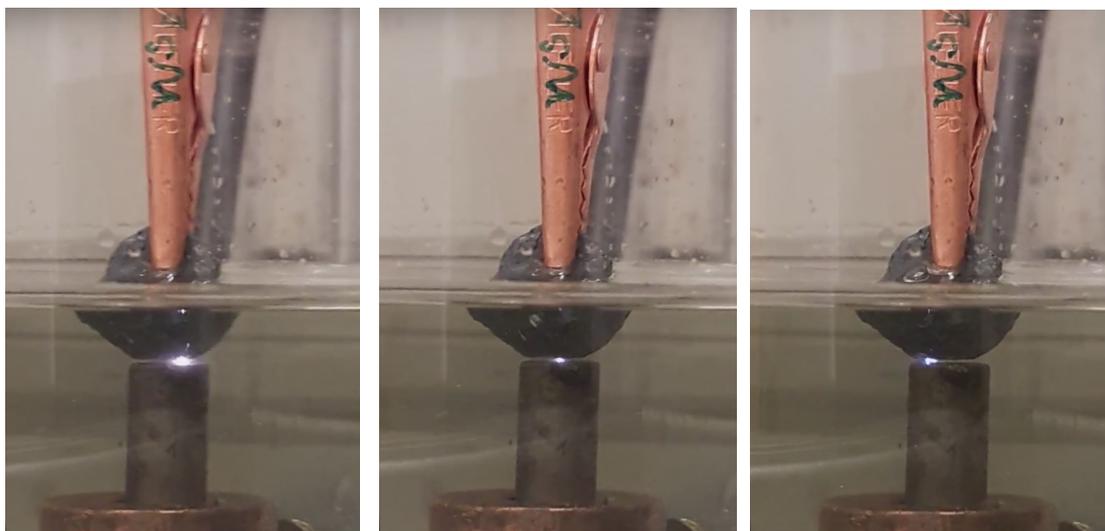
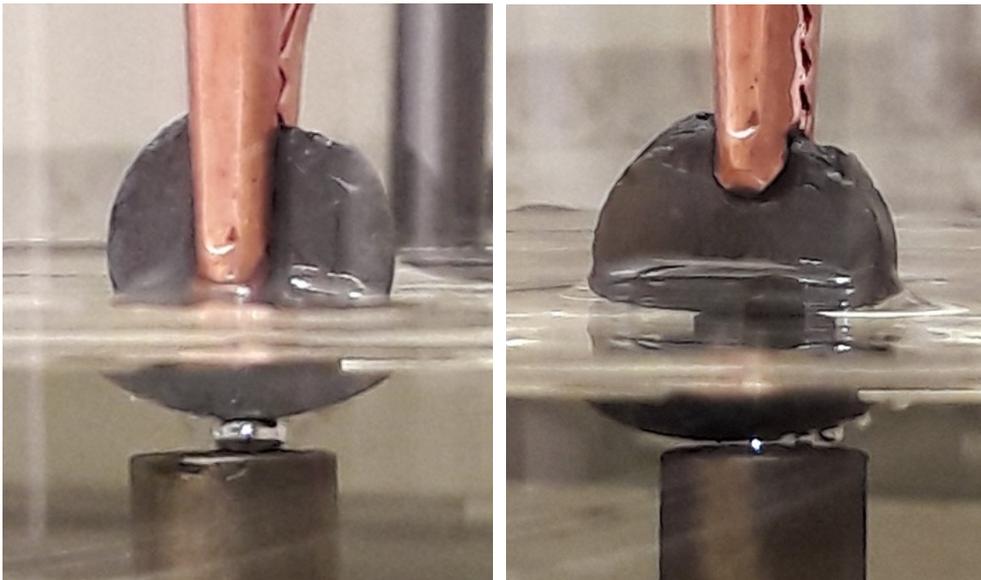


FIGURE 3.17: Flickering discharges along a  $WS_2$  disk.

In figure 3.18 A, a gas bubble is visible around a constant spark. This bubble comes from the vaporization of the dielectric liquid. In figure 2.2, a schematic drawing of the phenomena shows how the center of the discharge makes a plasma channel and around it a vapor bubble. The vapor could either be fully evaporated oleic acid, which is held close to the discharge because of the high energy release there. It could also be gas molecules from the different elements of the oleic acid. The high energy of the discharge may break the bonds of the oleic acid molecules and they may then react and create new molecules which are in gas phase in room temperature or higher, as around the spark. When the discharge ceases this gas could escape into the air. This escape could also happen during a constant spark. In figure 3.18 B small gas bubbles can be seen to the right of the discharge. These travel from the spark and out into the air.



(A) The vapor bubble created around the discharge. (B) Small bubbles escaping from the discharge to the right.

FIGURE 3.18: The dielectric liquid is vaporized around the plasma channel.

Other scenarios did take place during the process which are harder to explain. In figure 3.19 a discharge occurs at the side of the disk, creating an arc towards the bottom electrode. A hypothesis of why this happen is that the liquid was very dynamic at this time. It had just been poured into the beaker and bigger pieces of the disk were flushed around. With this turbulent environment and with voltages applied about 10 kV, this discharge was the most favorable.

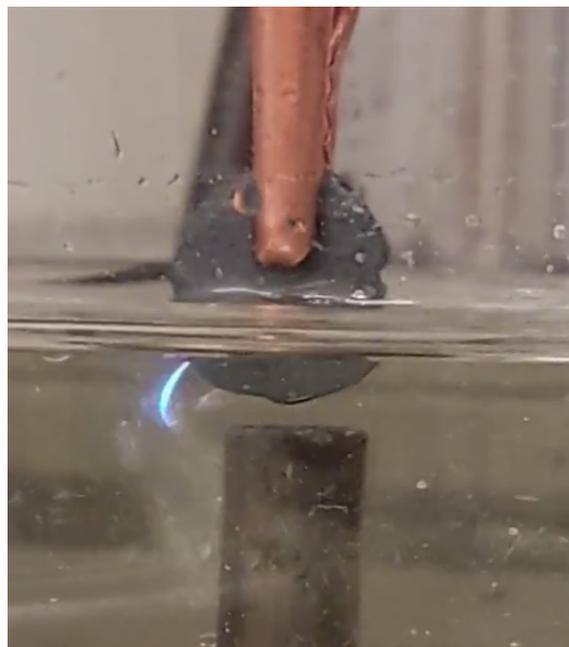


FIGURE 3.19: A discharge aiming from the side of a  $\text{MoS}_2$  disk to the side of the molybdenum rod.

### 3.4.2 Separation from oleic acid

The same centrifugation method as for the oil was applied to the oleic acid solution. The sample where  $\text{WS}_2$  material could be observed in the oleic acid was investigated. Different parameters of the centrifugation process were tried in order to clarify how the particles were separated easiest. Table 3.1 presents the work process for five different samples, all obtained from the same batch of oleic acid with  $\text{WS}_2$ . The main difference from the oil separation is that ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , was used for washing instead of isopropanol. This because the respective chemical was the easiest to dissolve in the respective dielectric.

During the process described in table 3.1 it was clear that particles were separated. Figure 3.20 shows a pellet made out of  $\text{WS}_2$  particles after the second centrifugation of sample 2. Similar pellets were observed for each sample after each centrifugation.

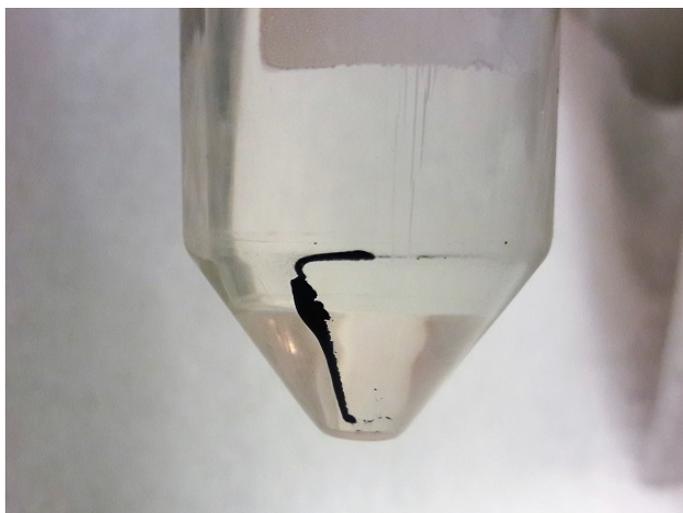


FIGURE 3.20: The pellet of  $\text{WS}_2$  particles at the bottom of the centrifugation tube.

The different samples were then added to gold coated wafers and characterized in SEM. Sample 1 was dripped on a wafer both before and after toluene was added. The other samples were used to produce one wafer-sample each, resulting in six wafers.

The SEM pictures for some samples are shown in figure 3.21. It can be concluded that the more start material of the oleic acid and  $\text{WS}_2$  solution, the more particles in the final solution. Sample 3 and 4 showed a very small amount of particles on the gold coated wafers, so no pictures from these are included. None of the samples diluted in toluene showed any oleic acid residues in these pictures, which means that three washing rounds, as for sample 5, is enough to get clean enough particles. The samples which had not been dissolved in toluene showed residues of the oleic acid. In figure 3.21 A and B, residues from the oleic acid are shown as amorphous areas with prominent charge effect. In figure 3.21 C and D, micro sized particles are shown without any bigger residues from the dielectric liquid.

### 3. Methods and results

TABLE 3.1: Centrifugation process of five different samples. OA means oleic acid, EtOH means ethanol and SN means supernatant.

Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Start material: 30 ml OA	Start material: 4.3 ml OA and 25.7 ml EtOH	Start material: 4.3 ml OA and 25.7 ml EtOH	Start material: 10 ml OA and 20 ml EtOH	Start material: 19 ml OA
Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 30 min, 6000 rpm
	Remove 5 ml, add 5 ml more OA	Remove 10 ml, add 10 ml more OA		Pour off SN, add 25 ml EtOH
Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm
Remove 25 ml, add 25 ml EtOH	Remove 25 ml, add 25 ml EtOH	Pour off SN, add 30 ml EtOH	Remove 25 ml, add 25 ml EtOH	Pour off SN, add 20 ml EtOH
Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 20 min, 6000 rpm	Centrifuge 15 min, 6000 rpm
Remove 20 ml, add 20 ml EtOH	Remove 20 ml, add 20 ml EtOH	Pour off SN, add 30 ml EtOH	Remove 20 ml, add 20 ml EtOH	Pour off SN
Centrifuge 40 min, 6000 rpm	Centrifuge 40 min, 6000 rpm	Centrifuge 40 min, 6000 rpm	Centrifuge 40 min, 6000 rpm	
Pour off SN, add 20 ml EtOH	Pour off SN	Pour off SN	Pour off SN, add 30 ml EtOH	
Centrifuge 30 min, 6000 rpm			Centrifuge 20 min, 6000 rpm	
Add EtOH so- lution to wafer and pour off SN			Pour off SN	
Dissolve in 1 ml toluene and add to wafer	Dissolve in 1 ml EtOH and add to wafer	Dissolve in 1 ml toluene and add to wafer	Dissolve in 1 ml toluene and add to wafer	Dissolve in 1 ml toluene and add to wafer

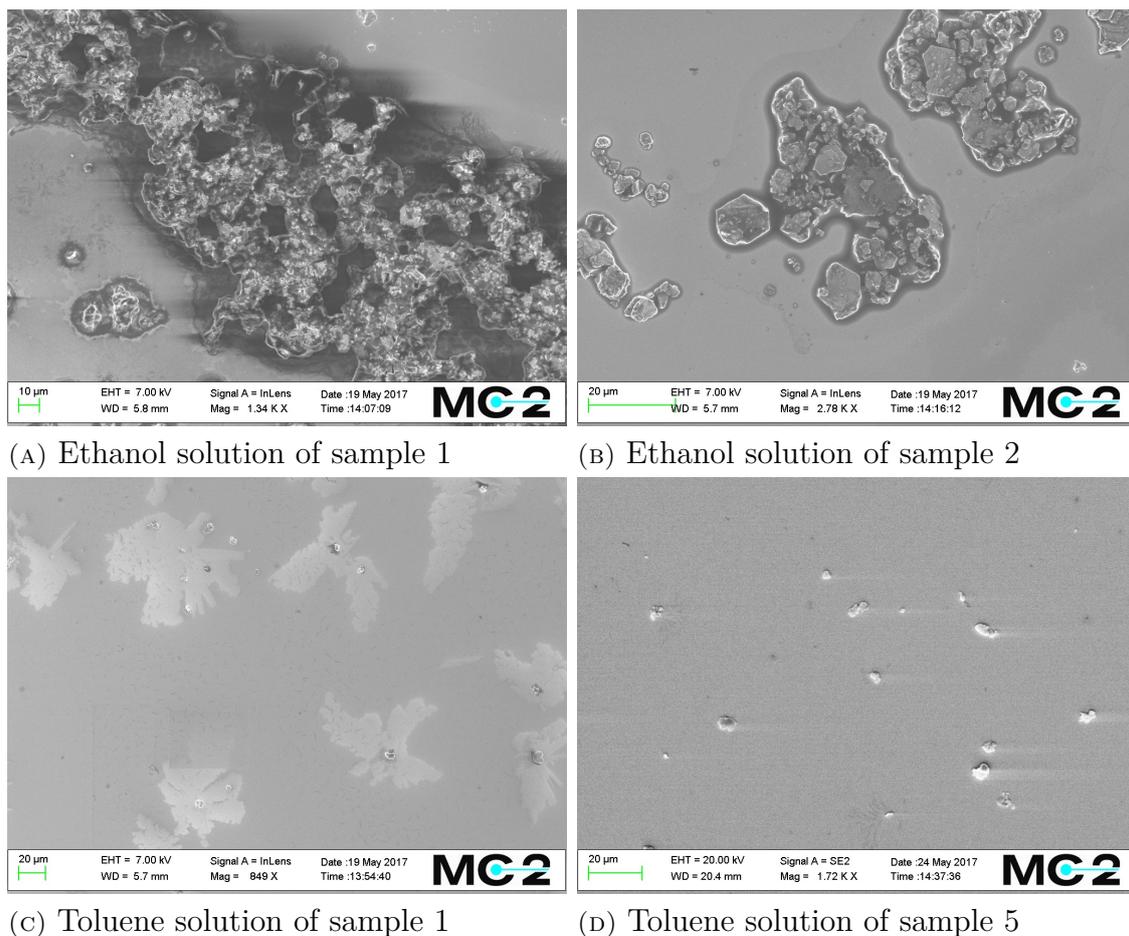


FIGURE 3.21: SEM pictures of four different wafers produced from sample 1, 2 and 5.

The microparticles observed on the gold coated wafers were examined in EDX and concluded to consist out of the two relevant elements: W and S. Figure 3.22 shows an EDX scanning of one of these microparticles. The signal is very weak and the background noise was large, meaning that this result is not very reliable.

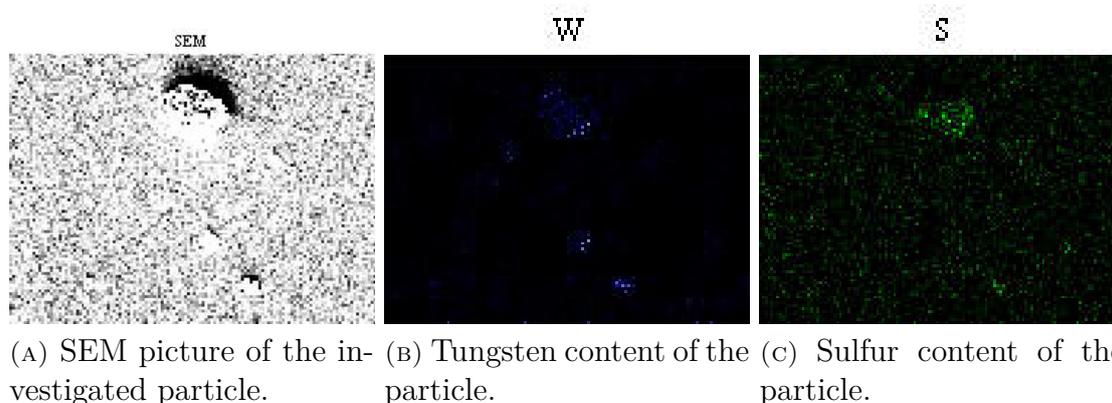
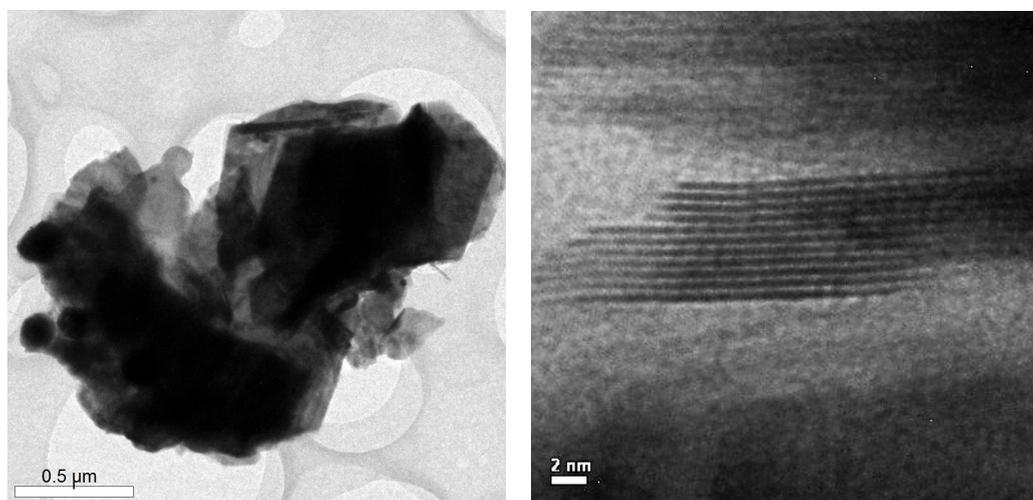


FIGURE 3.22: EDX of a particle found on the toluene solution of sample 1. The signal is not very clear and it had extensive background noise.

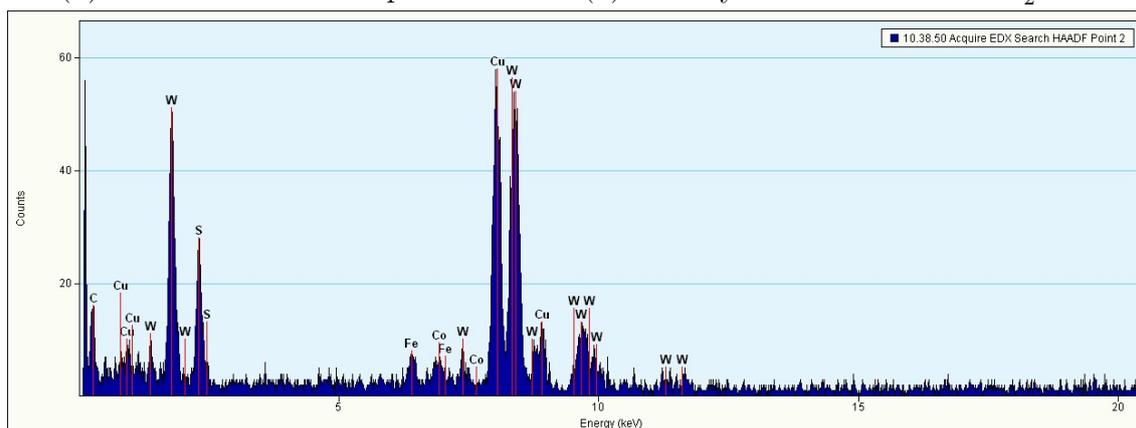
### 3. Methods and results

The toluene solution of sample 1 was also observed in TEM, dripped on a carbon coated copper grid. This provided more detailed pictures and element measurements of the microparticles. It showed that the particles were both  $WS_2$  particles and some contaminations, mostly iron and silicon, elements used in the spark machine before these experiments were conducted. The  $WS_2$  particles did consist of a various amount of sulfur,  $S$ , and tungsten,  $W$ . Figure 3.23 shows one of the investigated particles. The data corresponding to the EDX measurement (figure 3.23 C) is shown in table 3.2. Figure 3.23 B shows a typical pattern that could be seen all over the particle. It is the layered structure of bulk  $WS_2$ . This indicates that the particle consist of multilayered  $WS_2$ , some parts as thick as  $2 \mu m$ . The difference in sulfur content in the particle implies that even though layered structure could be seen, it is not possible that the entire particle consisted out of only these  $WS_2$  layers. It might also be parts with pure tungsten or as least with a very small amount of sulfur.



(A) Overview of a microparticle.

(B) The layered structure of  $WS_2$ .



(c) EDX measurement of present elements. The copper peak comes from the copper grid.

FIGURE 3.23: Examination of one particle found in the TEM. This is a  $WS_2$  particle.

TABLE 3.2: The composition of a particle examined with EDX.

Element	Weight %	Atomic %	Uncert. %
C	4.94	28.78	0.56
S	4.91	10.71	0.25
Fe	2.27	2.84	0.20
Co	1.88	2.24	0.20
Cu	31.51	34.68	0.77
W	54.47	20.72	1.22

Another particle had the composition shown in figure 3.24. It did not give any count for sulfur meaning that this particle contains a very small amount of sulfur and a very big amount of tungsten. This means that spark erosion changed the composition of the material, giving particles with different amounts of sulfur and tungsten.

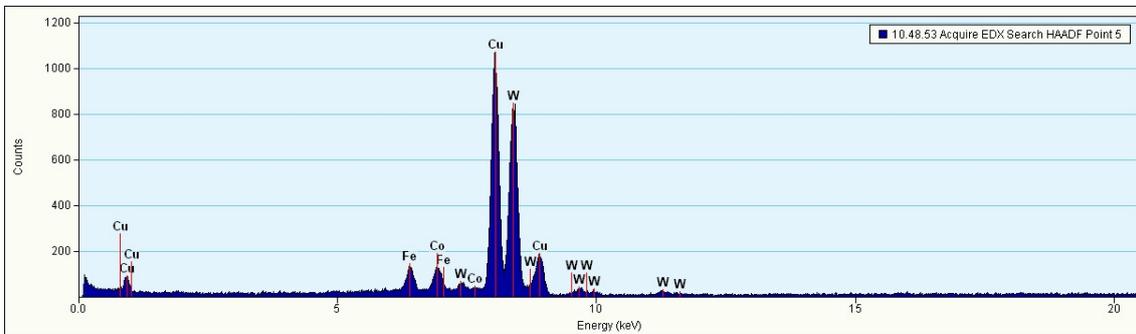


FIGURE 3.24: EDX measurement of one of the particles.

On sample 1 after dissolved in toluene, crystal branches were observed that stretched out from the micro particles. Figure 3.25 shows these in detail. It was believed that they could be two dimensional flakes, exfoliated in the spark erosion process. Why they were deposited on the gold surface as branches connected to the microparticles is not clear. One hypothesis is that they got deposited like that as the liquid (toluene) dried off and closed up towards the microparticles.

### 3. Methods and results

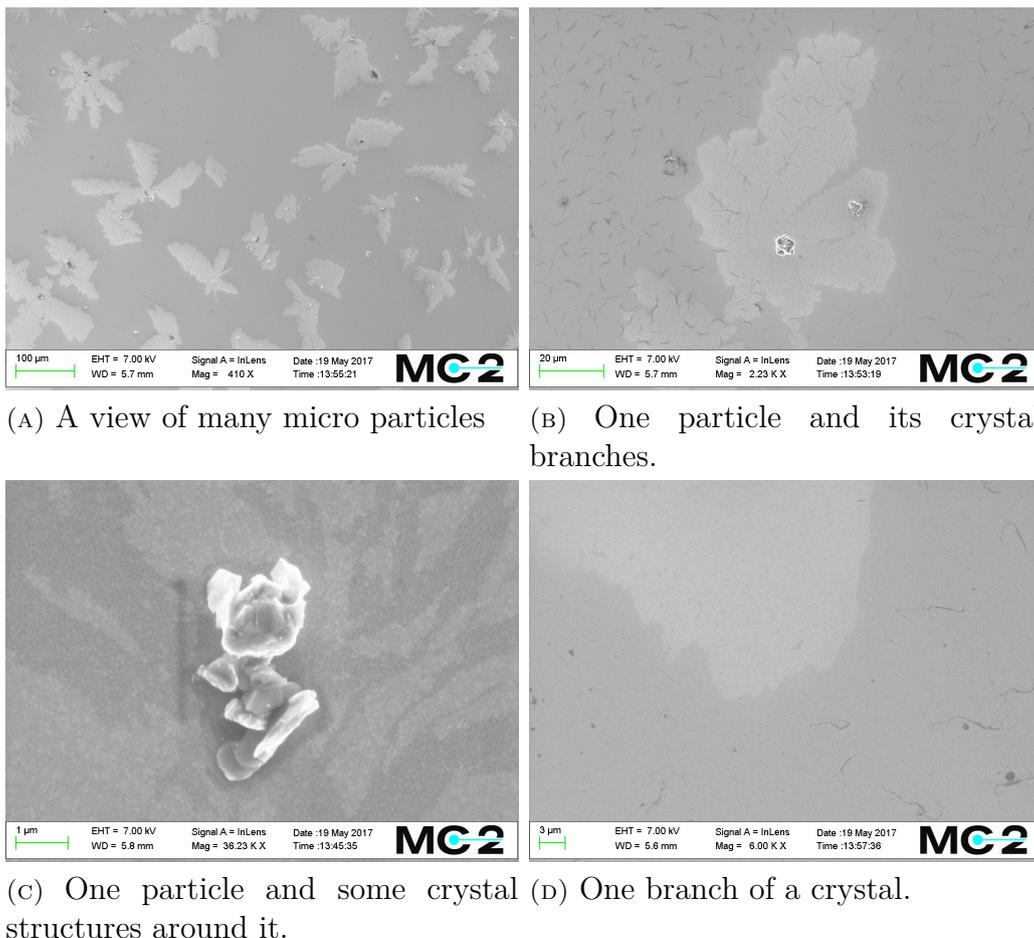


FIGURE 3.25: The crystal branches from sample 1 dissolved in toluene shown in detail.

This specific sample was then investigated further with Raman spectroscopy. The peaks observed when aiming on one of the micro particles are shown in figure 3.26. These peaks are typical of bulk  $WS_2$ , as presented by Berkdemir A. *et.al.* [38]. No peak for single layer  $WS_2$  was observed. The hypothesis that the crystal branches in figure 3.25 are 2D flakes could not be further supported. It is likely that they are residues from the oleic acid.

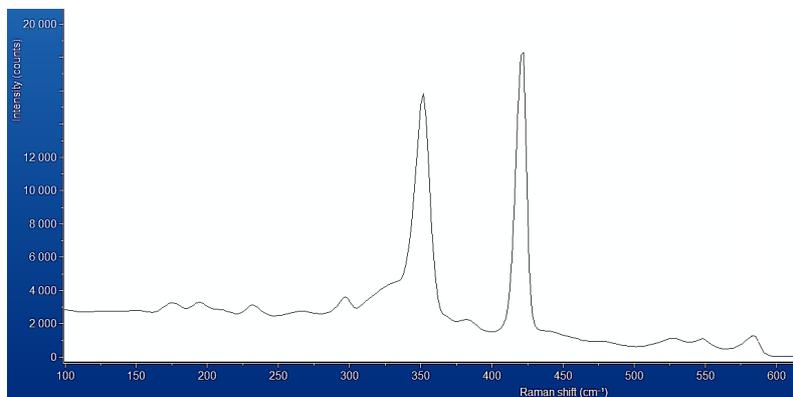


FIGURE 3.26: Raman spectroscopy measurement of a  $WS_2$  particle of sample 1.

# 4

## Conclusion

The results shown in the project are not enough to conclude if semiconductor 2D material could be produced using spark erosion. But there are some results that could be further discussed in order to have a first assessment about the method.

The energy of the spark is probably not enough to exfoliate the semiconductors into 2D material. There was only one compound,  $\text{WS}_2$ , which got successfully exfoliated. The hypothesis is that the other two requires higher energy of each spark in order to get melted or sublimated and then get dissolved in the dielectric liquid. A combination of higher current as well as high voltage could be implied for future experiments. It will result in higher energy of the spark which might overcome the energy it takes to sublime the  $\text{MoS}_2$  and  $\text{MoSe}_2$  materials.

The size of the exfoliated particles is around  $6 \pm 5 \mu\text{m}$  in diameter. They behave and look like bulk material of  $\text{WS}_2$ . This does also imply that the energy of the spark was too low. Higher energy is believed to produce smaller particles. Since the particles observed here are micro-sized, higher energy is needed in order to produce nano-sized particles.

An early hypothesis of this work was that the discharge would exfoliate the material by penetrating between the layers and therefore make it exfoliated layer by layer. As implied by the results of this work, it is not possible. When the plasma hits the disk it melts or evaporates the material. When it goes back to solid state, nucleation effects tends to make the particle spherical or at least not two dimensional.

Since the experiments are performed in oleic acid recombination effects of the produced particles could occur. This could be another reason why most particles observed are microsized and not nanosized or two dimensional. To counteract the recombination a surfactant could be added to the oleic acid. This would then keep the particles separated but it might make the separation from the liquid harder.

## 4. Conclusion

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The composition of the produced particles showed varying amount of tungsten compared to sulfur. This was concluded from data given from EDX measurements. Since the EDX data is not very reliable, neither are these conclusions. But if in fact the particles have different compositions, it means that the spark erosion process will modify that. When the discharge melts or vaporizes the material, even the covalent bonds between tungsten and sulfur may break. This would result in that the elements move, for a short time, away from each other and may form areas with higher concentrations of tungsten and sulfur respectively.

It may be possible, with further investigations, to tune the energy of the spark so precisely so that it is just enough to break van der Waal-bonds, but not covalent bonds. This might then result in that the material gets exfoliated only along the weak bonds, but not along the strong bonds, resulting in single layer nanoflakes.

It is important to note that only a few of the experiments in this project has been repeated, meaning that the results are not verified. Especially the last trial of spark erosion with oleic acid, described in section 3.4, was not accomplished more then one time. Therefore thorough conclusions can not be drawn.

# Bibliography

1. Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *science* **306**, 666–669 (2004).
2. Butler, S. Z. *et al.* Progress, challenges, and opportunities in two-dimensional materials beyond graphene. *ACS nano* **7**, 2898–2926 (2013).
3. Chalmers University of technology. *Graphene appointed an EU Future Emerging Technology flagship* 2013. <<http://www.chalmers.se/en/news/Pages/Graphene-appointed-an-EU-Future-Emerging-Technology-flagship.aspx>>.
4. Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature materials* **6**, 183–191 (2007).
5. Lee, Y.-H. *et al.* Synthesis of Large-Area MoS<sub>2</sub> Atomic Layers with Chemical Vapor Deposition. *Advanced Materials* **24**, 2320–2325 (2012).
6. Jameson, E. C. *Electrical discharge machining* (Society of Manufacturing Engineers, 2001).
7. Berkowitz, A. & Walter, J. Spark erosion: A method for producing rapidly quenched fine powders. *Journal of Materials Research* **2**, 277–288 (1987).
8. Ferry, D. K. *Semiconductors Bonds and bands* (IOP Publishing, 2013).
9. Schaller, R. R. Moore’s law: past, present and future. *IEEE spectrum* **34**, 52–59 (1997).
10. Kolobov, A. V. & Tominaga, J. *Two-Dimensional Transition-Metal Dichalcogenides* (Springer, 2016).
11. Wang, Q. H. *et al.* Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature nanotechnology* **7**, 699–712 (2012).
12. Chhowalla, M. *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature chemistry* **5**, 263–275 (2013).
13. Kim, J.-Y. *et al.* Thermal and electronic properties of exfoliated metal chalcogenides. **31**, 3225–3227 (2010).
14. Cannon, P. Melting point and sublimation of molybdenum disulphide. *Nature* **183**, 1612–1613 (1959).
15. Haynes, W. M. *CRC handbook of chemistry and physics* (CRC press, 2014).
16. Eagleson, M. *et al.* *Concise encyclopedia chemistry* (Walter de Gruyter, 1994).
17. El-Mahalawy, S. & Evans, B. Temperature dependence of the electrical conductivity and hall coefficient in 2H-MoS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, and MoTe<sub>2</sub>. *physica status solidi (b)* **79**, 713–722 (1977).
18. Tsai, H.-L. *et al.* Exfoliated- restacked phase of WS<sub>2</sub>. *Chemistry of materials* **9**, 879–882 (1997).

19. Thakurta, S. G. & Dutta, A. Electrical conductivity, thermoelectric power and Hall effect in p-type molybdenite (MoS<sub>2</sub>) crystal. *Journal of Physics and Chemistry of Solids* **44**, 407–416 (1983).
20. Radisavljevic, B. *et al.* Single-layer MoS<sub>2</sub> transistors. *Nature nanotechnology* **6**, 147–150 (2011).
21. Peek, F. The law of corona and the dielectric strength of air. *Proceedings of the American Institute of Electrical Engineers* **30**, 1485–1561 (1911).
22. Schoenbach, K. *et al.* Electrical breakdown of water in microgaps. *Plasma Sources Science and Technology* **17**, 024010 (2008).
23. Pfeiffer, T. *et al.* New developments in spark production of nanoparticles. *Advanced Powder Technology* **25**, 56–70 (2014).
24. Böttcher, C. J. F. *et al.* *Theory of electric polarization* (Elsevier Science Ltd, 1978).
25. Berkowitz, A. *et al.* Amorphous soft magnetic particles produced by spark erosion. *Journal of Magnetism and Magnetic Materials* **254**, 1–6 (2003).
26. Jung, S.-H. *et al.* High-yield synthesis of multi-walled carbon nanotubes by arc discharge in liquid nitrogen. *Applied Physics A* **76**, 285–286 (2003).
27. Cabanillas, E. *et al.* Production of uranium–molybdenum particles by spark-erosion. *Journal of nuclear materials* **324**, 1–5 (2004).
28. Hector, L. & Schultz, H. The dielectric constant of air at radiofrequencies. *Physics* **7**, 133–136 (1936).
29. VEGA Grieshaber KG. *List of dielectric constants - VEGA 2015*. <[https://webcache.googleusercontent.com/search?q=cache:Lh2q\\_cYoilAJ:https://www.vega.com/home\\_ss/-/media/PDF-files/List\\_of\\_dielectric\\_constants\\_EN.ashx+&cd=3&hl=sv&ct=clnk&gl=se&client=firefox-b-ab](https://webcache.googleusercontent.com/search?q=cache:Lh2q_cYoilAJ:https://www.vega.com/home_ss/-/media/PDF-files/List_of_dielectric_constants_EN.ashx+&cd=3&hl=sv&ct=clnk&gl=se&client=firefox-b-ab)>.
30. ACD/Labs. *ChemSketch* version 11.0. 2017. <<http://www.acdlabs.com/resources/freeware/chemsketch/>>.
31. Hosking, M. *et al.* The dielectric constant of liquid nitrogen over the frequency range 0.5 to 10.4 GHz. *Superconductor Science and Technology* **6**, 549 (1993).
32. Bhattacharyya, B. *et al.* Electrochemical machining: new possibilities for micromachining. *Robotics and Computer-Integrated Manufacturing* **18**, 283–289 (2002).
33. Nanoscience Technology. *Scanning Electron Microscopy* 2016. <<http://www.nanoscience.com/technology/sem-technology/>>.
34. The University of Iowa. *Transmission Electron Microscopy* 2012. <<https://cmrf.research.uiowa.edu/transmission-electron-microscopy>>.
35. Russ, J. C. *Fundamentals of Energy Dispersive X-Ray Analysis: Butterworths Monographs in Materials* (Butterworth-Heinemann, 2013).
36. Bowley, H. J. *et al.* *Practical raman spectroscopy* (Springer Science & Business Media, 2012).
37. SHT Smart High Tech AB. 2017. <<http://www.sht-tek.com/>>.
38. Berkdemir, A. *et al.* Identification of individual and few layers of WS<sub>2</sub> using Raman Spectroscopy. *Scientific reports* **3** (2013).

# A

## Appendix 1

Below three thorough descriptions of the spark erosion process will be presented. Each of them is performed with oleic acid as dielectric liquid and the high voltage supplier as the power source. Each description describes one TMDC in the following order: MoS<sub>2</sub>, MoSe<sub>2</sub> and WS<sub>2</sub>.

### A.1 Detailed description of spark erosion with MoS<sub>2</sub>

May 11<sup>th</sup> 2017      MoS<sub>2</sub> disk, 250 ml oleic acid

Discharge initiated 09.22, 6.6 kV induced a constant spark for two minutes. Then just a few flickering sparks for one minute. Then constant spark for two minutes and then the electrodes got connected by small pieces of the disk falling into the gap.

Higher the disk 1 mm produced some flickering sparks which pushed away this material. Lower the disk again led to a few sparks. Then it all stopped.

Raise voltage to 8 kV, few sparks and then nothing.

Raise voltage to 9 kV, few sparks and now more often. 09.38 started a constant spark. 09.46 the sparks flickered a lot. 09.52: very few sparks.

Thought: *More and faster flickering of the spark feels more effective. Constant sparks looks less powerful than a instant spark.*

Raise voltage to 10 kV gives faster flickering sparks again. Very good until 10.16, then it became constant.

10.18 flickering sparks. 10.35 very rarely occurring sparks. 10.38 nothing.

Higher the disk above the liquid and wiping of the surface facing the bottom electrode. Did not help, still no sparks.

Thought: *No difference is seen in the liquid or on the disk. After one hour of discharges something should be seen as a confirmation of exfoliation.*

Adjust the electrode distance to less than 0.3 mm. Spark occurred again at 10.45 with voltage applied of 3 kV. Gives a very small, constant spark. 10.48 the electrodes got connected.

Higher and lower the disk 1 mm gave constant spark. Raising voltage to 5 kV does not give a difference. 10.51 the electrodes got connected.

Similar scenarios like this until 11.20. Experiment turned off.

Thought: *No change in colour of the oleic acid and no visible effect of the surface of the disk. Even though discharges occurred most of the time for two hours, still no change was observed.*

## A.2 Detailed description of spark erosion with MoSe<sub>2</sub>

May 11<sup>th</sup> 2017      MoSe<sub>2</sub> disk, 250 ml oleic acid

The disk was very brittle. As soon as the clamp putted pressure on it, small parts of it fell off. Therefore the electrodes were easily connected to each other with material from the disk.

Discharge initiated 14.40. Constant plasma channel until 14.46. Then a little flickering and then they got connected by pieces of the disk. Higher and lower the disk 1 mm led to that the material was removed and led to a constant spark for some seconds, then they got connected again.

Thought: *Connection of the electrodes feels more likely of a brittle disk. Not only because the mechanical handling breaks of parts of it, but also because it looks like the sparks makes a powder of the disk. This powder looks like the initial powder used for compressing the disks. It is produced in small amounts, sometimes not at all, and falls down into the gap between the electrodes.*

14.48, after removal of the material in the gap, a constant spark was initiated for 8 kV.

Similar procedures were made until 15.20. Very good flickering sparks at this moment for 30 minutes.

Connected again at 15.56. Higher the disk 2 mm led to a big spark that pushed away all the disturbing material. When lowered a small constant spark was observed. 16.14 connected again.

Similar procedures were made until 16.40. Experiment turned off.

Thought: *No change in colour of the oleic acid and no visible effect of the surface of the disk. Even though discharges occurred most of the time for two hours, still no change was observed.*

## A.3 Detailed description of spark erosion with WS<sub>2</sub>

May 12<sup>th</sup> 2017      WS<sub>2</sub> disk, 200 ml oleic acid

Discharge initiated 09.33. After a few small sparks a bubble is created around the plasma channel which is somehow conducting. It also looks like smoke around it.

Long and flickering discharges were shot towards the air and long the sides of the disk.

Thought: *The deviating events of the discharges here is probably due to a very dynamic environment. The oleic acid was poured into the beaker short before the voltage was applied and material from the disk, mechanically teared off by the clamp, were floating around.*

Electrode distance was adjusted to be very short, less than 0.3 mm, and a spark was initiated at 5 kV. Better, flickering sparks at 6 kV at 09.45.

09.48 the electrode distance could be bigger, hard to see with bare eyes. Raise voltage to 9.7 kV, many random sparks.

9.50: very rarely sparking for voltage of 10 kV. From 10.10 nothing.

Adjusting electrode distance, few sparks again at 10.21 at 10 kV.

Adjusting electrode distance and acquired a good distance at 10.25. Flickering sparks at 6.5 kV. Raise voltage to 8 kV at 10.32.

9 kV at 10.42 gave very good flickering sparks.

The setup could be left alone for longer times with flickering sparks. 11.02 adjusting of distance. 11.11 connected, higher and lower the disk. Flickering sparks initiated again.

Similar procedures were made until 11.30. Experiment turned off.

Thought: *The liquid was significantly darker. Also the lower part of the disk was flatter and blacker. Does this mean that particles were produced?*