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Synthesis of 2-D nanostructure of Bismuth Oxychloride

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SUBJECT: Independent Project Report

Abstract

This project studies the synthesis process of 2-D nanostructure of Bismuth oxychloride (BiOCl). The experiment involves synthesis of BiOCl particles and its exfoliation steps. BiOCl will be synthesized from Bismuth Nitrate (Bi(NO₃)₃) or Bismuth Chloride (BiCl₃) with water, and Hydrochloric acid (HCl). Synthesized particles will be dispersed in Methyl Amine-Methanol solution and subjected to sonication for exfoliation. The purpose of the experiment is to successfully obtain monolayered structure of BiOCl and test its electrical properties such as conductivity. All measurements of the experimental data will be taken using optical microscope, scanning electron microscope (SEM), and Raman spectroscopy.

Introduction

The main objective of this project is to create a single-layer structure of BiOCl and see its properties. Since the founding of the graphene, two-dimensional nanostructures and its application to semiconductors, sensors, and batteries had been widely studied due to its unique properties such as high surface-volume ratio. In this project, we are investigating the two-dimensional nanosheet structure of Bismuth, which, due to its high atomic number, may show more stability than carbon, and see and compare its properties to other materials such as graphene. While there are ways to achieve such structures, in this experiment liquid exfoliation technique was chosen using methyl amine-methanol solution as solvent. Due to its similar surface tension, ideally with certain amount of energy applied, the solvent can break the weak van der waals between the layers and yield mono-layer nanosheet of BiOCl. The main problem with this procedure is that it requires extensive period of time of sonication. Since methyl amine has very low boiling point, the vapor pressure builds up quickly in the room temperature. Thus, during the sonication, the vapor pressure gets too high and occasionally break the microcentri.tube, letting outside materials such as water into the container, contaminating the process. To prevent this, the solution size has been modified from 1mL to 10mL and container was replaced to 20ml glass vial with screw cap. Sample was deposited on clean Silicon wafer and glass to be observed. All observation was made using optical microscope.

Methods

In this experiment, BiOCl was synthesized in two different size: 1 µm and 10 µm. For the 1 µm BiOCl, 10 mmol of BiCl₃ was dissolved with 100mL of ethanol in 400mL beaker. The solution was stirred until all BiCl₃ powder was dissolved. While stirring, 100mL of distilled water was added for the reaction, and 1mL of Hydrochloric acid afterwards to set the reaction pH. The reaction is spontaneous and exothermic, and the white powder begins to form as the reaction goes. After 2 hours, the solution was set on the table top for 6 hours without stirring. White particles was visible on the bottom of the beaker. The particles was collected and washed with water and ethanol. The particles were dried using the vacuum furnace with 40 ºC. The particles were collected and stored. Collected particles were dispersed in ethanol and drop casted on the silicon wafer for particle size examination (Figure 1).

For the 10 µm BiOCl, 1 mmol of Bi(NO₃)₃ was dissolved in 5mL of Hydrochloric acid in 400mL beaker. 200mL of distilled water was added to the solution. The solution was
stirred on the VWR advanced hotplate stirrer (VWR, Radnor, PA) with the temperature of 120 °C. White powder begins to form in the solution. After 4 hours, the solution was set to rest on the table top for 6 hours. White particles were visible on the bottom of the beaker. The particles were collected and washed with water and ethanol. Washed particles were dried in vacuum furnace with 40 °C. The particles were collected and stored. Collected particles were dispersed in ethanol and drop casted on the silicon wafer for size examination (Figure 2).

For the exfoliation of BiOCl, 5 different concentration of methyl amine-methanol solutions were prepared varying 1M to 5M. For 1 µm BiOCl particle, 10mg BiOCl was dissolved in 10 mL of respectable methyl amine-methanol solution. The vial was subjected to sonication step in Branson Ultrasonic Cleaner 2510 (Branson Ultrasonics, Danbury, CT) for 1 hour. 20 µL of solution was drop casted on the silicon wafer and examined under the microscope. The solution was centrifuged with 3000rpm for 10 minutes. The liquid was discarded and same concentration of 10 mL methyl amine-methanol solution was added. The sonication and drop casting step was repeated. For 10 µm particle, the process was replicated from the 1 µm BiOCl exfoliation but instead of having 10mg/10mL solution, 1mg BiOCl/1mL methylamine-methanol solution was used for the sonication step. All samples were drop casted on silicon wafer and examined under the microscope.

Results and Discussion

As shown in figure 3, no visible nanosheet structure were found under the microscope for the 1st exfoliation step of 1 µm BiOCl particle. However, after the 2nd exfoliation step, several nanosheets or exfoliating nanosheets were visible under the microscope. It is shown that more exfoliated sheets were visible with exfoliation step with higher concentration of methyl amine-methanol solution than lower concentration. No furthur development
were found with extra exfoliation step. For 10 µm BiOCl particle, optical image of exfoliated sample are shown in figure 4. Nanosheet structures were easily found in the samples in the higher concentration of methyl amine-methanol solution.

*Figure 4. Optical image of exfoliated of 10 µm BiOCl*

For the smaller particle size, the volume and mass of the sample was ten times larger than that of larger particle size. Since the exfoliation requires sonication steps to transfer enough energy to break the Cl-O epitaxy bond, it is safe to assume that larger volume requires larger power for it to have same amount of nanosheets as larger particles. Since the same exfoliation steps were adapted to both of the particles, lesser nanosheet density as shown in figure 3 than figure 4 is reasonable. Plus, since the particle was ten times larger than the other, the size of the exfoliated sheets were considerably larger and it was easier to locate when using optical microscope.

On the other hand, with 10 µm BiOCl sample, unusual salt crystal was visible on the sample. We are currently investigating the identity of the crystal, but it is suspected to be nitrate impurities survived in the crystal washing step. Another step of ethanol washing will be conducted before the next or new exfoliation.

For the future, exfoliation of BiOCl using different solvent such as methanol or ethanol will be tested and see compare its effectiveness.