THE WINSTON CHURCHILL MEMORIAL TRUST OF AUSTRALIA

Report by - Sivacarendran Balendhran - 2014 Churchill Fellow

TO CREATE HIGH PERFORMANCE ELECTRONIC MEMORY DEVICES BY COMBINING EXOTIC TWO-DIMENSIONAL MATERIALS

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Signed Sivacarendran Balendhran Date 31/07/15
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EXECUTIVE SUMMARY

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Project description: This project aims to develop high performance electronic/memory devices by combining exotic two-dimensional (2D) materials together. The Churchill Fellowship enabled the fellow to travel MIT, USA to learn the processes involved in synthesising such 2D materials for memristors.

Project highlights:

- Learning the processes involved in the synthesis of large area 2D materials for making sandwich structures of two different materials.
- Training on the state of the art synthesis/characterization facilities and establishing such capabilities back in Australia (at RMIT University)
- Adapting the research practices used in a top tier university and implementing it back in Australia
- Attending Materials Research Society Fall 2014 meeting to gain knowledge on the recent developments in the field and to establishing international collaborative networks.

Major lessons and conclusion:
Synthesis technique was successfully established to grow large area few layered MoO₃ crystals in a high vacuum vapour deposition system. Based on these skill set an ARC Discovery Early Career Researcher Award ($360,000 for three years) was secured to implement the 2D memristor project. This project facilitates 2 PhD candidatures which have already commenced. From the knowledge gained and the acquired ARC funding, a brand new high vacuum, chemical vapour deposition system similar to that of MIT, has been set up at RMIT and to be commissioned soon.

Extensive skillsets gained in new characterization equipment, efficient laboratory training and waste disposal practices that are currently being adopted here at RMIT. Opportunities were provided to take part in other projects such as signal transmission in plant cells, material synthesis, low-temperature electronic transportation etc.

Research work conducted during the period will be disseminated through journal articles and conference presentations (one co-authored journal article (under review) and two lead author journal articles under preparation).
PROGRAMME

18/10/14 – 19/12/14 (9 weeks) : Research work at Strano Group, Department of Chemical Engineering, MIT, Cambridge, USA.

30/11/14 – 05/12/14 (1 week) : Conference attendance at Materials Research Society Fall Meeting 2014, Boston, USA.

20/12/14 – 04/01/15 (2 weeks) : Personal family time-off in Los Angeles, USA
**THE FELLOWSHIP**

*What is a two-dimensional material?*

We live in a three dimensional world where things are made out of atoms and everything has a length, width and a height (or depth). Even the thinnest cat whisker has a thickness, as it is made out of billions of atoms. To compose the tangible things we see, atoms tightly bind to each other in all three dimensions (Figure 1a), like a Rubik’s cube, where each of the coloured block is bound to the neighbouring ones, in all three dimensions. But there is a class of layered materials which can be compared to a stack of paper (that has length, width and height). Here the atoms are tightly bound only along the length and width dimensions while along third dimension they are simply stacked and sitting on top of each other (like a stack of paper). As they are very weakly coupled they can be separated as easily as picking a single paper off a stack. Such a single planar layer of atoms are considered to be two dimensional.

![Figure 1](image.png)

*Figure 1*  
(a) Cubic diamond crystal structure, the 3D form of carbon [I].  
(b) Graphite crystal structure, the layered form of carbon [II].

*Why two-dimensional materials?*
In 2004, the most famous 2D material graphene (a single layer of carbon), was extracted from a graphite crystal (the material used in pencils) by using sticky tape to peel it off.\textsuperscript{1,2} The scientists who achieved this also showed that these 2D layers demonstrate enhanced electronic properties compared to their 3D counterpart (transport properties thousands of times larger).\textsuperscript{1} What this meant was if we have such 2D materials replacing today’s silicon based electronics, we could have computers that run 100 times faster than today’s computers, while only consuming a fraction of the power. The scientists who conducted this experiment (Konstantin Novoselov and Andre Geim) won the Noble Prize in Physics in 2010 for this revolutionary discovery. As this phenomena is still relatively new in comparison to silicon technology (which is more than 60 years old), it has not yet been pioneered.

\textbf{What are memristors?}

Today’s memory devices remember 1s and 0s based on charge storage and require electricity for this. A memristor is a passive electronic element which remembers its previous electrical state indefinitely. This was a conceptual device that existed for over 40 years and was experimentally realized only 8 years ago. Here 3D metal oxide thin films (typically in the order of 100 times thicker than 2D materials) are utilized to make such memristors. This class of first memristor devices are still at their infancy.

\textbf{The proposal}

This project aims to combine the enhanced transport properties of two dimensional materials to create memristors that can be extremely fast and energy efficient. The goal is to replace the 3D metal oxide films with 2D materials which will cut down the thickness by at least 100 times. Such a reduction in thickness would translate into higher memory
density. The favourable transport properties mean faster reading and writing times in resistive memories, made of such memristors.

**The bottleneck**

Although two dimensional materials are capable of delivering such exceptional device performances, large scale processes of synthesising high quality 2D materials remains to be a main hurdle to overcome. Mechanically peeling individual layers provides high quality pristine crystals, but it’s a low yield process and cannot be adopted for an industrial scale production of devices. Figure 2 shows a 2D molybdenum trioxide (MoO₃) crystal acquired from mechanically peeling a bulk crystal. They can be easily identified by the fact that they don’t possess a shadow or a boarder caused by the illumination of the microscope light. As seen from the figure, these crystals are too small (the scale bar is 0.02 mm) and the probability of obtaining them are very low. Hence this method is not feasible.

![Figure 2](image-url)  
**Figure 2** | Optical microscope image of mechanically peeled MoO₃ crystals.
The solution

Chemical vapour deposition (CVD) is a technique that is used in growing large area graphene and MoS$_2$. $^{4,5}$ Prof. Michael Strano is one of the leading chemists and expert who pioneered in the synthesis of 1D (carbon nanotubes) and 2D (graphene) phases of carbon. Strano Research Group at MIT houses some of the best, purpose built, high vacuum CVD equipment. The main goal of this research trip was to use this facility to produce large area 2D crystals of MoO$_3$ and set-up a similar CVD facility back at RMIT University. This would enable us at RMIT University to grow various 2D crystal structures to pursue the development of 2D memristor devices. Figure 3 illustrates the two main purpose built equipment that was utilized for this purpose at MIT.

![Figure 3](image)

**a.** Cryogenic chamber that cools the material down to -265 °C to study the transport properties. **b.** A high vacuum CVD system with a multi-zone furnace that reaches up to 1200°C.

The experiment

The experimental work involved heating MoO$_3$ powder at high temperatures till it evaporates and the vaporised MoO$_3$ would be flushed to the growth area using the flow of argon gas. At the lower temperature downstream area, growth substrates are placed for the
vaporized $\text{MoO}_3$ to grow into highly ordered 2D crystals. Ideal crystal growth temperature and pressure were experimentally determined over multiple trials. Figure 4 illustrates the experimental setup.

![Figure 4](image)

**Figure 4** | a. Furnace incorporating the evacuated quartz tube b. magnified image illustrating the precursor and growth substrate setup.

The results

The crystals generally nucleate at random sites and cover the lateral 2D area and then they keep bulking up into multiple layers. The goal here is to control the growth so that the whole lateral area is covered while preventing it from bulking up into multiple layers. Figure 5a shows the initial experiments done at ambient pressure where the growth didn’t cover the whole area, instead they started growing vertically. This case was overcome by evacuating the tube down to high vacuum (Figure 5b). Several trials later by tuning the growth temperature and duration a dominant 2D crystal coverage was established (Figure 5c), while suppressing multilayer growth. However, there were still voids seen as the area coverage was still not perfect. Eventually after weeks of trials and errors large area coverage was established (Figure 5d).
Figure 5 | Microscope images showing the evolution of successful large area 2D MoO$_3$ crystal growth. The images are a summary of weeks of experimental work leading to an established recipe (depending on temperature, pressure, gas flow rate and growth duration) for the growth of large area 2D MoO$_3$.

Atomic force microscopy (AFM) is a technique that is used to map the surface of materials down to single atomic layer thicknesses. The AFM images acquired on the as grown crystals clearly show that these are in fact 2D crystals at a few fundamental mono-layers. Figure 6 shows the cross sectional profile of such a crystal. The thickness profile indicates that the crystals are composed of about 8 fundamental atomic layers of MoO$_3$ octahedra.  

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Figure 6 | Atomic force microscopy image of the surface profile of the as grown crystals. The cross sectional profile of the crystal indicates the achievement of 2D crystal growth.

Although AFM profiles indicate atomically thin 2D crystals, it does not confirm the composition of these crystals. Micro Raman spectroscopy is a technique where materials are excited with a powerful laser and resultant atomic vibrations due to this excitation are captured using a detector. Depending on the bonds that are present in a particular material structure, the atoms vibrate in unique ways. As a result each individual material has its own Raman signature. This technique can be used to identify the composition of the resultant crystal growth.

Figure 7 indicates the micro Raman spectra acquired on the as grown 2D MoO$_3$ crystals. The peaks observed at 284, 666, 821 and 996 cm$^{-1}$ correspond to various molybdenum–oxygen bonds stretching, due to the energy received by the laser excitation.$^5$ This is a signature characteristic of highly ordered layered $\alpha$-MoO$_3$, and thus it is confirmed the as grown crystals are in fact perfectly ordered MoO$_3$. These structures will be used as the growth substrates for other types of already established 2D materials such as MoS$_2$, creating sandwich structures of two different 2D materials.
Figure 7 | Raman spectrum of the as grown samples. The signature Raman peaks at 284, 666, 821, 996 cm\(^{-1}\) indicate the presence of highly ordered MoO\(_3\) crystals.

Lessons learnt

- Large area 2D crystal growth:

  CVD technique was applied and perfected to synthesise large area 2D MoO\(_3\) crystals. I was able to gain knowledge and expertise in establishing a high vacuum CVD system. Upon returning back I was able to assemble a similar, if not better high pressure CVD system at RMIT University (Figure 8). During the fellowship, the time I spent collaborating in other projects, allowed me to gain knowledge in growing various types of 2D materials and sandwich structures of MoO\(_3\) with graphene and MoS\(_2\). Based on the acquired expertise, we would be able to synthesise various types of 2D materials not only for memristor applications but also for other electronic and optoelectronic research that is being conducted here at RMIT University.
Figure 8 | Purpose built high vacuum, multizone CVD system at RMIT University.

- Semiconductor parameter analyser setup/training:
  I had the opportunity to utilize a system with a cryogenic chamber that allows reaching temperatures of up to -263 °C, coupled with a parameter analyser which measure transport properties of 2D materials at such temperatures. A same type of parameter analyser is set to be procured in 2016 to upgrade the current capabilities of the Functional Materials and Microsystems Research Group at RMIT. Such a capability is invaluable for electronic device development and would be of utmost importance in the 2D memristor project.

- Photocurrent mapping using atomic force microscopy:
  A purpose built laser excitation source coupled with an AFM is utilized to study the optoelectronic properties of 2D materials.

- Extended training/workshop in laboratory safety, laser safety and hazardous waste disposal:
Recurring training classes that can be readily enrolled an attended depending on the requirement of the employee at MIT. Such established programs can be easily adopted and incorporated into our own existing programs for improved standards.

- MRS Fall Meeting 2014:
  I had the opportunity to listen to some of the pioneering material scientists such as Prof. Mildred Dresselhaus, Prof. Jonathan Coleman, Prof. Manish Chhowalla delivering their research. It was both inspiring and intellectually stimulating. I was also able to learn about the latest developments in the field of material science and engineering. I also had the opportunity to network, promote my research and establish new collaborations (UCLA, NTU and A*STAR Singapore)

- The CVD synthesis of 2D MoO$_3$ crystals and characterization is currently under preparation as a journal article. Electronic device transport properties of liquid phase exfoliated 2D MoO$_3$ crystals were investigated at cryogenic temperatures (at –263 °C). These exciting results are currently under review in the scientific journal *Nature Nanotechnology*. Another exotic 2D material, phosphorene, which was seeded at MIT, is currently being studied for its excellent electronic and mechanical properties. This work is almost complete and is also currently under preparation to be submitted to a suitable scientific journal.
CONCLUSIONS AND RECOMMENDATIONS

The fellowship was a great learning experience in terms of gaining new skillsets as well as experiencing a completely different research culture. The expertise gained during the fellowship was applied to establish similar research capabilities back here at RMIT University. The collaborative network built is a crucial element in ongoing research as well as future research projects that are to be commenced soon. The MRS Fall meeting facilitated the opportunity to network and promote our own research work in an international arena.

Currently as an ARC Research Fellow, I’m privileged to lead the 2D memristor project for the next 3 years. There are two PhD students undertaking their candidature based on this research project. In terms of research and training, I’m able to filter the advantages and disadvantages of both research practices that I have experienced and pass it on to my students. Also some of the already established laboratory safety/waste disposal practices that I learnt at MIT are being implemented here at RMIT.

Research record keeping strategies are much more lenient here in Australia and are generally a choice based option for individual universities. Some of the already established successful processes can be adopted as minimum standard of record keeping strategies and should be strictly enforced in Australia.

Dissemination of the project outcomes will be in the form of peer reviewed scientific journals as well as to be presented in international conferences both in Australia and overseas. The intellectual properties developed during this project will be patented with the help of RMIT University. The research progress achieved will be delivered to the general
public through organisations such as Royal Society of Victoria, Churchill Trust as well as online and printed media outlets.

REFERENCES


