

MRS Talk

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OK, thank you very much. Good morning everyone. My name is Jacob, I'm a grad student at Trinity College Dublin, and I'm very happy to be here today to speak to you about the effects of argon:oxygen plasma treatment on MoS₂.

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In case you're not familiar with the topic, here's a quick primer:

Pure oxygen plasma likes to form MoO₃ by replacing sulfur from the MoS₂ lattice. This hampers device conductivity and causes p-type doping.

In the case of pure argon, there's no chemical reaction, but we have physical sputtering of sulfur. This has recently been used to induce a 2H to 1T polytype shift in single layer MoS₂.

For our experiments, we tested what happens when we mix the two gases in the plasma cleaner.

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So here are some examples from the literature:

You can see the drain-source current drops heavily with plasma time in the case of pure oxygen, same with carrier mobility.

Whereas for pure argon we can see this metallic flat response in the gate curve after treatment.

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Here's our data for a 4 layer back-gated sample. We ran the IV and gate sweeps every 2 seconds, and saw this unusual jump in the conductance at 6 seconds. This was then followed by a large drop for subsequent exposures.

In the gate sweeps, at 6 seconds in red, we start getting more current all across the gate bias. We have a large threshold voltage shift to negative biases. This persists even after 8 and 10 seconds. Then we have another threshold shift back to positive gate bias and a large drop in the conductance.

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Plotting the mobility for all gate biases, we notice this recovery at 6 seconds in the linear region.

As we track it over time, at 6 seconds we get a series of these recovery peaks. This is followed by a large drop-off in the mobility and no further recoveries.

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To understand this better, we investigated the morphology of the surface.

The AFM phase maps begin to show some material contrast over time.

We also start seeing patches of dark contrast in the SEM, which may initially suggest etching.

However, looking at the height of the flake we see that it increases, while its surface remains highly flat.

This is unusual, but has been reported before.

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We did some spectroscopy to see which oxides the plasma forms on the surface.

The Raman spectra of the 4 layer sample show heavy quenching as we increase the plasma time.

Meanwhile, the PL emission hits a critical point at 6 seconds and we get a massive boost in the yield of direct recombination.

We think this is due to the top layer decoupling optically from the rest of the stack due to oxygen intercalation.

With increasing time, the emission then quenches due to defects.

EDX mapping shows us that we are increasing in oxygen content, relative to the sulfur, in a linear fashion over time.

This is visualised by increasing pixel count in these oxygen maps.

XPS spectra show the increasing content of MoO_3 on the surface of the sample.

Over time, the trioxide becomes more stoichiometrically complete, as those doublet peaks get narrower.

The sulfur doublet, in turn, broadens significantly as sulfur is removed from the surface.

Both spectra are shifted heavily to higher binding energies at 6 seconds. That correlates with the n-type doping that we saw in the transfer curves.

So whatever is present on the surface at 6 seconds looks to be responsible for the doping.

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We did some electron microscopy to have a closer look at the surface after plasma treatment.

So here on the left, we have some HRTEM images of MoS_2 as it reacts with the plasma over time.

At longer treatments, we begin to see these regions of amorphous material forming on the surface.

We get some complex contrast changes that are not so easy to interpret in the TEM, so we tested our samples in the aberration corrected STEM.

Here we have a bilayer region that's received some damage from the plasma after 6 seconds.

There's some serious damage in this region here, but more importantly all across the surface we see these small etched pits.

There are hundreds of them, even just in this field of view, and when we go to have a closer look...

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...we see two types of voids in this bilayer.

The one in orange is a perforation that has no material left in it, while the red one has only had the top molecular layer removed.

Their size increases over time and some of them even merge with other pits to form bigger ones.

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With EDX and EELS in the ACSTEM after 6 seconds, we see no oxygen. This is quite odd, because previously we saw plenty of it in the freshly treated samples.

We found that if we keep the sample under ultra high vacuum overnight, the oxides desorb from the surface.

We can actually reverse the recovery phenomenon, by keeping the sample in vacuum for a long time.

The boosted gate curve returns to close to its original pre-plasma state when left overnight in a vacuum chamber.

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So here's a sketch of what we think happens.

At 6 seconds, we form this pseudo-metallic two-dimensional oxide on the top layer.

It does not contribute much surface roughness, but increases the height of the flake due to the presence of oxygen.

The argon creates a lot of sulfur vacancies in the material, which end up causing a significant amount of negative charge to be present in the underlying MoS_2 layers.

The scattering potential is then effectively screened by the presence of this metallic layer.

So we're able to carry the current more efficiently from source to drain, and we don't need as high a gate field to open the channel, as we're now closer to the gate oxide.

The subsequent drop in the mobility and conductance is due to the increasing amount of defects and the completion of the insulating MoO_3 phase in the top layers.

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So to sum it up:

We observed an unusual 2D phase of substoichiometric MoO_3 , which forms on the surface of MoS_2 and enhances its carrier transport.

We find that it is different from the usually reported insulating MoO_3 in both electrical and physical properties.

And we hope that it can be exploited in future van der Waals heterodevices to improve electrical performance.

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So I'd like to thank all our collaborators at Trinity College who were involved in this project.

Thank you for listening; if you have any questions I'll be happy to answer.