Methods of Graphene Transfer

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Motivations

- Graphene growth can be scaled using Chemical Vapour Deposition (CVD) onto copper.
- Generally, we want to use graphene on substrates other than copper, primarily SiO_2/Si.
- Efficient, high-fidelity transfer method for graphene required.

Current Process

1. Coat the graphene in PMMA.
2. Etch away the underlying copper.
3. Wash the PMMA-graphene in water.
4. Scoop the PMMA-graphene layer with the desired substrate.
5. Dissolve the PMMA in acetone.

Problems in the Current Process

- Differences in surface geometry of the growth and target substrates cause cracks.
- The etchant introduces residues and impurities in the transferred graphene.
- PMMA sometimes leaves residues in the graphene.

Solutions

Making PVA Solutions

- PVA dissolves in a temperature window of 70-85°C. Higher temperatures cause denaturation.
- PVA needs to be added slowly and stirring needs to be strong and constant.
- The solution thickens around 6% *(w/v)* and saturates around 7% *(w/v)*. This spin-coats well at 2000 RPM.
- Glycerol dissolves readily into this solution at room temperature with mild stirring.
- PVA layers cure around 110°C, in about 10 minutes.

Peel-Offs

- Graphene peeled onto both commercial PVA and PVA solution has good continuity.
- Using a glass or Al_2O_3 backing for PVA-solution graphene makes it easy to handle.
- The PVA-graphene attraction is too strong to transfer the graphene.
- Dunking in liquid nitrogen releases graphene, but doesn't transfer it to a substrate.

Peel-Offs

PVA-glycerol

- Adding glycerol to PVA decreases the adhesion between PVA and graphene, until glycerol conc. is around 1% *(v/v)* in 7% PVA.
- This does not translate to an increased adhesion for the PVA graphene stack to SiO_2.
- Using a glycerol-IPA solution in the peel-off makes the PVA film very sticky, and hard to handle.

Peel-Offs

- Spin-coating with PMMA, and peeling off with Kapton tape works, but the Kapton-PMMA layer does not dissolve fully in acetone or other solvents.
- Paraffin does not allow peel-offs, as the attraction is not strong enough. [1]

Bubble Delamination

- Requires an inert electrode, like graphite, to prevent other ions.
- Only paraffin and PMMA handles can be used, as PVA will dissolve.
- There are two possibilities:
  - Oxidise the copper, and then reduce it at $\sim$ -1.8 volts.
  - Place the copper at $\sim$ -2.6 volts. This causes ions to intercalate between graphene and copper. [2]
- Both were quite unreliable and hard to diagnose.

Paraffin Residue.

- It dissolves readily in toluene, which needs to be washed off in IPA, but leaves a blue residue layer. Heating to 90°C does not help.
- Strong heating at $\sim$ 400°C after dissolving helps remove residue, but also erodes the graphene.
- Heating the paraffin to 400°C directly after the transfer leaves a very incomplete layer.

Electrochemical Etching

- Copper can be electropolished, or dissolved, at $\sim$ 6 volts, using H_3PO_4 as electrolyte.
- We can use this method to remove the copper without the need for an etchant.
- However, the copper dissolution is patchy, and a better fixture is required.
- Upon applying 12 volts, rapid bubble delamination also occurred.

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References

[1] Wei Sun Leong et al. Paraffin-enabled graphene transfer. *Nature Communications*, 10(1):867, Feb 2019.

[2] Ken Verguts et al. Graphene delamination using 'electrochemical methods': an ion intercalation effect. *Nanoscale*, 10:5515–5521, 2018.