IPS14 Discussion Notes

August 4-6, 2014

This is the transcript of questions and discussion contributions after presentations and in the dedicated discussion sessions of the IPS14 symposium at MSU, http://nanotube.msu.edu/IPS14/

Snapshots of the whiteboard with the notes are posted at http://nanotube.msu.edu/IPS14/gallery.html

The notes have been taken and transcripts have been provided by Zhen Zhu and Jie Guan of MSU.

IPS14 Discussion Topics
(Yuanbo Zhang)

- Effective mass as a function of thickness of black phosphorus;
- Electron affinity as a function of thickness;
- Levi's book on layered materials, 1980s
- Exfoliation in air?
- Contrast as a function of wavelength/thickness
- Work function of contact
- How much light the sample see in the process/how to avoid this.
- Mobility anisotropy depend on temperature?

IPS14 Discussion Topics
(Yuanbo Zhang)

- Annealing method, like heater near the sample
- How soon to fabricate the device/coating by PMMA
- Single layer data?
- Why black phosphorus is p-type
- Switch voltage varies for different sample.
- Degradation surface in bulk
- Limiting for mobility
- Thickness dependence of carrier concentration
- Hysteresis during I-V, due to absorbate

IPS14 Discussion Topics
(Gotthard Seifert)

- P nanotube? Semiconducting?
- Electronic structure of different allotropes?
- How to keep the other allotropes stable at regular pressure?
- Stacking? Are they inter-locked in different stacking?
- Metal insulator transition?
- Cubic structure transition due to Peierls?
- Covalent modification to phosphorene?
- Related to instability of phosphorus? O_2,H_2O?
- High pressure → cubic phase?

IPS14 Discussion Topics
(Gotthard Seifert)

- DFTB for phase transition?
- Hydronated graphene counterpart to black phosphorus?
- Phosphrus nanotube, electronic structure?
- Prospect for synthesis? catalyst? Ball-milling?
- Six-ring structure in cluster phase?

IPS14 Discussion Topics
(Mark C Hersam)

- Depth of degradation? Will it go deeper or just on the surface? (on the surface)
- General 2D material? Could it change the material of hydrophilic to hydrophobic if change the edge?
- How good is AlO_x encapsulation?
- How thick is the AlO_x layer? (30nm) Temperature? (room temperature) Pressure? (1Torr)
- XPS, deal with AlO_x capsulation layer?
- AFM is done in air?
- Relationship of roughness vs time? (Initial bubble is not related to the degradation, no XPS peak.)
- Why degradation is coming from side?

IPS14 Discussion Topics
(A S Rodin)

- Binding energy of excitons
- Any thing about antimony and bismuth
- The method does not consider z-direction? How many layers could be dealt with in such model?
- Comparision with bulk data?
- 1D and 2D, transferable?
- How to extend to 3D,buk black-P

IPS14 Discussion Topics
(Mildred Dresselhaus)

- Band gap value? (monolayer gap ≈2.0eV)
- Notation of vibration mode not universal decided. Need to use same notation
- Phosphorene? Whether proper? Phosphane?

IPS14 Discussion Topics (C1)

- Compare phosphrene to other materials?
- Is it a good thermoelectric material? Contact material: Pt
- How many device? Large scale application?
- Response time? How fast?
- Photo stability? PMMA passivation last a month.

IPS14 Discussion Topics (C2)

- Mobility of 2nm sample? How stable?
- Peak in mobility as thickness change?
- Source of black phosphorus?

IPS14 Discussion Topics (C3)

- Why intensity decreases when oxidization happen?
- Why there is no oxygen related peaks? Not Raman active?
- TEM image of amorphous structures?
- Capping layer? PMMA structures?
- Raman through capping layer?
- Other technique to reveal degradation?
  - XPS, FIRI?
  - Other method to monitor the degradation?

IPS14 Discussion Topics
(C5)

- How to get monolayer? Well prevented from O_2,H_2O
- Could Raman spectra see the inter-layer interaction?

IPS14 Discussion Topics (C6)

- How rough is phosphorene?
- Why passivation could give better transport results?
- Passivation affect hole mobility?
- Electron mobility is low?
- Sandwich structure?

IPS14 Discussion Topics (C7)

- Quality of the samples made by liquid exfoliation
- How stable of the samples
- Amorphous 2D-P
- Could the rotated phosphorene few layers similar to few layer graphene
- Application of the liquid exfoliated phosphorene
- Productivity , sonication and shear mixer
- Size distribution of phophorene produced
- Did you see decrease in lateral dimension when increase sonication speed

IPS14 Discussion Topics (C8)

- Energy for inducing phase transition?
- Nomenclature
- Symmetry of different phases?
- DFT energy reliable?
- Can only pressure produce other phase? Conditions to produce selective phases?
- Band gap changes due to strain in few layer P?

IPS14 Discussion Topics (C9)

- Chiral index of PNTs
- Why metal-insulator transition?
- Absorption of oxygen? Degradation?
- Bismuth nanotube? Why it is easier than P to form?
- Energy vs strain in PNTs
- Whether different functional will change the transition change?
- Take use of negative poisson ratio?

IPS14 Discussion Topics (C10)

- Metal contact? (Au/Ti)
- Time delay of preparation and device measurement?
- Second best mobility? (10nm thick)
- EDS maping substrate? (silicon)
- Whether gold will accelerate the degradation?
- Strain? (Bending, less than 2%)
- Degradation makes sample more conductive or not?
- Degradation at the edge, surface or side modification? Intercalation?
- Intercalation/degradation mechanism may be different for bulk or <5nm thickness

IPS14 Discussion Topics
(C10)

- Thin layer capping, e-beam lithography ≈5nm
- E-beam evaporation evaporate Al instead of AlO_x
- Degradation starts from edge?

IPS14 Discussion Topics (C11)

- How to show the orthogonal properties of electronic/thermoelectronic properties
- Why the ZT is so large?
- Is thermal and electronic conduction decoupled?
- Single-layer thermoelectric may be not very useful?
- Fundamental band gap? Effect of substrate? Suspended? Comparison to GW results.
- STM/STS work on phosphorus/single layer or few layer? Mechanic exfoliation/liquid exfoliation

IPS14 Discussion Topics (C11)

- Twisted bilayer phosphorene layers →different electronic properties as “real” bilayer.
- Substrate effect to 2D material → “ARPES” for phosphorene
- Photo-electron emission microscopy

IPS14 Discussion Topics (C12)

- Whether Raman could measure the compression along “c” direction?
- QMC for graphene and phosphorene compared?
- Why QMC is trustable in exfoliation energy?

IPS14 Discussion Topics (C13)

- Why Si/Tin should be planar and 2D?
- Why fluoride tin? TI, large gap

IPS14 Discussion Topics (C14)

- Phosphrene self-healing in the edge. Reconstruction
- Phosphorus oxygen defects? O is not saturated, compare with phosphorus oxide
- Hydrogen passivation depends on T and P
- Atomic level self-assembly to form graphene nanoribbon
- If edge is not perfect, transport calculation?

Monday afternoon discussion

- Degradation
  - M does not change if thick enough (>5nm), (only surface affected)
  - Degradation process with O_2,H_2O is not uniform, not clear where it starts.
  - Degradation by intercalation can occur. (see I.3)
    - JPC 116,14772(2012), Li intercalation in b-P.
  - Protection
    - PMMA good only for N>3 layers
    - BN full encapsulation may be better
    - Parylene-C passivates bi-layers

- Degradation
  - Degradation by oxidation, role of defects?
    - A. Ziletti, arxiv, O defects in phosphorene
    - Oxidation does not need structural defects for nucleation, but grows. (G. Seifert, A. Ziletti)
    - XPS may tell us the state of oxygen binding
    - Few nm Al_2O_3 does not prevent degradation, ambient may penetrate from side
    - Oxidation is an activated process, 0.5eV activation needed, due to magnetic state of oxygen
    - EELS shows only P, O signature, shows also intermediary states of oxygen adsorption
    - Oxidation requires both O_2 and H_2O
    - XPS: 20% oxidation in 100% O_2; 3% oxidation in H_2O, but pH>7 should react (C.17 poster)
    - No extra Raman peaks occurred in O_2 degraded samples

- Degradation
  - Degradation by other chemistries?
    - C-P bonds?
    - Phosphorites, P-O-Cchain→ phosphoric acid
    - DCTS should identify degradations

- Monolayer b-P device?
  - Not yet
- Protection by phosphoric acid?
  - Can top layer be converted to acid and self-protect?
  - No, etches through
- Doping
  - Sn, I_2 are present in commercial samples: (American elements), (2D semiconductors)
  - Use Augez, SIMs to qualify doping
  - Undoped samples are p-type at room T and ambipolar at 77K
  - N-doping with Te (Morita, Appl. Phys A 39,227(1986))
- Growth
- USTC grows samples in a well-defined way, but is P-type
  - Commercial companies do not reveal synthesis process

Tuesday afternoon discussion

- Hope for electronics with phosphorene?
  - Need better on/off ratio than 10^5 so that it is useful in the fab. (will give 10^4)
  - Is flexibility of the channel so useful? (need 20% stretchability)
  - Is phosphorene superior to organic electronics? CNTs? Amorphous Si? TMDs?
  - Short-channel effects speak in favor of 2D electronics
  - Contacts to 2D are more difficult than 3D
  - Mobility >100 is good
  - Hysteresis passivation eliminate it

- Hope for electronics with phosphorene?
  - Off current: 10^{-3} is too high, maybe defect-related
  - Ambipolarity
  - Probably fully encapsuated monolayers are best
  - Sub-threshold swing
  - Reproducibility for large-scale production
  - Hope for optoelectronics?
  - Useful for IR detection due to large band gap, direct
  - Try ball milling to make phosphorene, ink. Band gap?
  - Ultrafast device/communications?
  - Danger of non-uniformity of samples

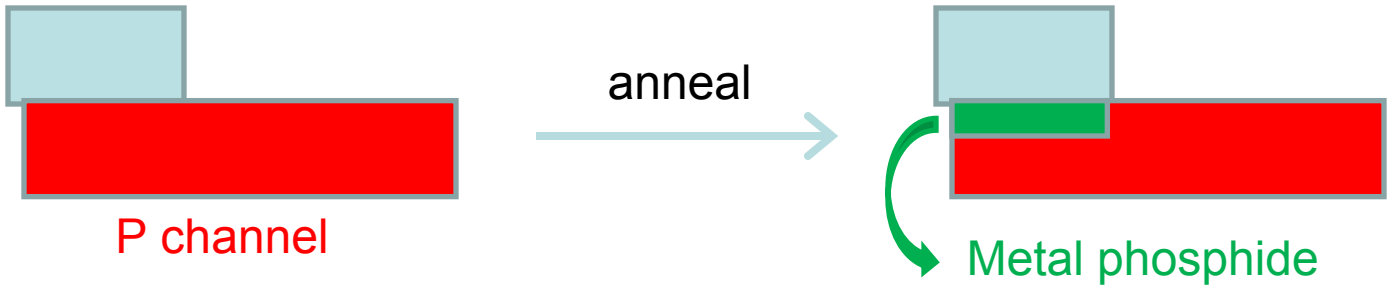
- Potential killer application?
  - “Best” 2D electronics?
  - Fun material, very different from graphene, TMDs.
  - Potential for low-cost/ low performance electronics
  - Photovoltaics?
  - Promising optical properties?
  - Need large-area monolayer/layer controlled phosphorene
  - CVD?
  - MBE?

Wednesday discussion

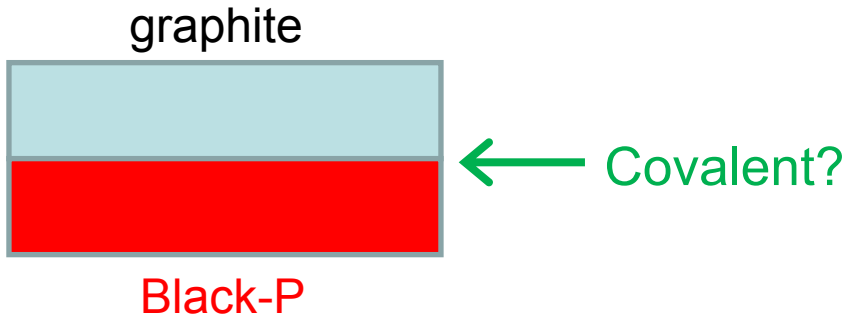
- IPS15?
  - Candidate locations:
    - MSU <<< selected
    - Paris-France
    - Shanghai-China
  - Conflicts/time
    - Early August 2015
    - Potential conflicts:
      - » ACS Fall
      - » GRC
      - » ICPS (in Austin in 2014)
    - Y-H Lee is in charge of selecting dates
  - Funding/grants
    - Chongwu Zhou, NSF/ONR/AFOSR
    - Jeanie Lau, DARPA
    - Li Yang, NSF

- IPS15?
  - Help with abstract formatting:
    - Scott Warren
    - Gotthard Seifert
  - Reidentify sorting categories
    - Alexandre Favron
    - Liangbo Liang

- Electrical contacts
  - Ni/Au, Ti/Au, Cr/Au for d>4nm
  - When d<<4nm, gap opens, schottky/tunneling barrier problem
  - Oxidation of channel and contact is increasing contact resistance
  - Formation of phosphide phases. Can it form at low enough T?
  - Which metal will contact to p-type P, and which metal will contact to n-type P.



- Junction with other materials
  - Black-P/MoS_2 gives p-n junction
  - Graphite/black-P (Yi Cui et al. Nano Lett. 2014)



- (large-scale) synthesis
  - Physical exfoliation
  - Chemical exfoliation
  - CVD: substrate/conditions?
  - MBE, will go to P_4? PH_3?
  - Theoretical guidance: pressure, T, substrate
  - Important of lattice matching
  - Can black-P form by annealing metal-phosphide, similar to SiC→graphene?
  - Need compounds, cohere other component has higher vapor pressure and does not leave first
  - GaP, InP?
  - Groth on Sn? Tom Lange, Snilges
  - Electronic processes, similar to CNT formation?

- Applications of black-P beyond channel material
  - Thermoelectric applications? Limited due to instability
- Transport calculation
- Structural changes induced by different exfoliation techniques
- Spin-orbit coupling
- Surface chemistry
- Electron-phonon interaction

- Uniqueness of black-P with other 2D systems? Physics? Application?
- What type of defects and how dangerous for transport?
- Grain boundaries/dislocations?
- Doping/intercalation
- Properties of edges
- Effect of environment (substrate) on band gap?
- Quantum hall effect? H-field effect?
- Degradation/passivation