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 $\rightarrow$ cubic phase?
IPS14 Discussion Topics
(Gotthard Seifert)

– DFTB for phase transition?
– Hydronated graphene counterpart to black phosphorus?
– Phosphorus 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 ≈ 2.0 eV)
- Notation of vibration mode not universal decided. Need to use same notation
- Phosphorene? Whether proper? Phosphane?
IPS14 Discussion Topics (C1)

- Compare phosphorene 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 $\text{O}_2, \text{H}_2\text{O}$
– 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 mapping 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?
- STM/STS work on phosphorus/single layer or few layer? Mechanic exfoliation/liquid exfoliation
IPS14 Discussion Topics (C11)

- Twisted bilayer phosphorene layers \(\rightarrow\) different electronic properties as “real” bilayer.
- Substrate effect to 2D material \(\rightarrow\) “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)

- Phosphorene 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$_2$O 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$_2$O$_3$ 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$_2$O
    • XPS: 20% oxidation in 100% O$_2$; 3% oxidation in H$_2$O, 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 encapsulated 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.

![Diagram showing P channel and metal phosphide after annealing process]
• 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$\rightarrow$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