PCSI
Room Canyon/Sugarloaf - Session PCSI-1WeA
Devices and Contacts

Moderator: Alex Demkov, The University of Texas

2:00pm **PCSI-1WeA-1 Towards Fermi Level De-pinning at Contacts***, John Robertson,* Cambridge University, UK*; Y Guo,* Wuhan University, China*; Z Zhang,* Cambridge University, UK **INVITED**

Fermi level pinning at Schottky barriers (SB) strongly limits the reduction of contact resistances and thus scaling of modern electronic devices and future 2D semiconductor devices. We find that some complex semiconductor-metal interfaces with bonding configurations parallel to the interface create a type of localized interface or 'defect state' beyond the metal induced gap state (MIGS) model. Examples are interfaces between Si and metal disilicides and between Si and Sb. These defect states do not easily match to conventional MIGS and this mixes states of metal character into the surface pinning level. This creates Fermi level de-pinning and a variation of SB height with interface orientation.

The MIGS model [1] has successfully described many aspects of Schottky barrier behavior, including the slope of barrier height (SBH) with metal work function, S=¶φ/¶F_M and the charge neutrality level. However, it does not include several factors like interface bonding [2]. The MIGS model would say the S factor should depend only on metal work function, not type of metal (elemental or silicide/TiN) or on the face orientation, despite these being seen experimentally [2,3] and found in DFT supercell calculations [4]. We show that both metal silicides and Sb break the MIGS due to the presence of 'defect-like' states [5] at their interfaces, due to states which cannot be easily captured by the limited MIGS basis set of bulk semiconductor states. A metal-like character enters the effective CNL pinning energy, which also gives the orientation dependence. The chemically different case of Si:Sb behaves similarly to the silicides. These two factors are signifiers of Fermi level de-pinning, to find other examples.

[1] J Tersoff, PRL **52** 465 (1984)

[2] R T Tung, PRL **84** 6078 (2000); APR 1 011304 (2014); PRL.**5**2, 461 (1984); JVST. *B***1**1, 1546 (1993)

[3] T Nishimura, et al, APX 9 081201 (2016)

[4] L Lin, et al, APL **101** 052110 (2012); H Li, et al, Sci Report **7** 16669 (2017); J Robertson, SSDM (2018)

[5] H Fujitani, S Asano, PRB **50** 8681 (1994)

$^+$ Author for correspondence: jr214@cam.ac.uk

Figure 2 Showing 'defect state at Si:silicide (111), (100) interfaces causing the de-pinning and orientation dependence

Figure 1 Showing Fermi level depinning and face dependence in Si: silicide interfaces

2:40pm **PCSI-1WeA-9 Observation, Characterization, and Mitigation of the Internal *p-n* Junction in Pyrite FeS_2, a Potential Low-cost Solar Absorber***, Bryan Voigt, W Moore, J Walter, B Das, M Maiti, M Manno,* University of Minnesota*; E Aydil,* New York University*; C Leighton,* University of Minnesota

Pyrite FeS_2 is widely acknowledged as an ideal semiconductor for thin film solar cells due to its earth-abundance, low toxicity, low cost, suitable band gap (0.95 eV) and minority carrier diffusion length, and high visible light absorptivity. Power conversion efficiencies of FeS_2 heterojunction solar cells, however, have never exceeded 3% due to low open-circuit voltages (V_{OC} <0.3 V). One hypothesis emerging from recent temperature (*T*)-dependent transport of single crystals is that this low V_{OC} is due to a conductive pyrite surface with a carrier type (*p*-type) inverted from bulk (*n*-type) [1,2]. This could create a leaky (*i.e.*, low-V_{OC}) internal junction, thus limiting solar cell efficiencies. These studies established conduction through a 1-3 nm-thick, *p*-type surface upon freeze-out of *n*-type bulk carriers [1,2]. Two parallel resistors representing the surface and bulk can describe the *T*-dependence of resistivity [1] and the non-linear Hall effect observed near the crossover between bulk- and surface-dominated conduction [2]. Notably, what has neither been observed nor characterized, however, is the internal junction implied by this *p*-surface and *n*-bulk. Here, we directly observe this internal junction for the first time. In-plane sheet resistance (R_S) measurements of polished crystals doped heavily *n*-type *via* sulfur vacancies are shown to display an effect where metallic-like transport abruptly transitions to rapidly increasing R_S below ~175 K, eventually transitioning to surface conduction (at *T* <100 K). We show that this very unusual *T*-dependence can be well described by incorporating an exponentially-*T*-dependent junction resistance into the parallel resistor model. Junction barrier heights extracted from the model are typically 0.15 – 0.30 eV, in good agreement with typical V_{OC} values in past heterojunction solar cells, suggesting that this internal junction may, in fact, be limiting efficiencies. Interestingly, while its influence in $R_S(T)$ is independent of contact materials such as In, Ag, Fe, Co, and Ni, CoS_2 contacts mitigate this junction, allowing the first characterization of bulk properties to low *T*. Access to low *T* unveils rich phenomena, such as the onset of a smaller donor activation energy below 175 K, non-linear Hall effect near 100 K, and an unusual resistivity anomaly at *T* ≤10 K, showcasing CoS_2 contacts as a way to both mitigate this junction and advance understanding of electronic transport in FeS_2. This work was supported by the customers of Xcel Energy through a grant from the Renewables Development Fund.

[1] M. Limpinsel *et al.*, Energy Environ. Sci. **7**, 1974 (2014).

[2] J. Walter, *et al.*, Phys. Rev. Mater. **1**, 065403 (2017).

2:45pm **PCSI-1WeA-10 UPGRADED: Photo-Driven Dipole Reordering: Key to Carrier Separation in Metalorganic Halide Provskites***, Philipp Ebert,* Forschungszentrum Jülich, Germany*; H Hsu,* National Taiwan University, Republic of China*; B Huang,* Academia Sinica, Republic of China*; S Chin,* National Taiwan University, Republic of China*; C Hsing, D Nguyen,* Academia Sinica, Republic of China*; M Schnedler,* Forschungszentrum Jülich, Germany*; R Sankar,* Academia Sinica, Republic of China*; R Dunin-Borkowski,* Forschungszentrum Jülich, Germany*; C Wei,* Academia Sinica, Republic of China*; C Chen, Y Chiu,* National Taiwan University, Republic of China

Photo-driven dipole reordering of the intercalated organic molecules in halide perovskites has been suggested to be a critical degree of freedom, potentially affecting physical properties, device performance, and stability of hybrid perovskite–based optoelectronic devices. However, thus far a direct atomically-resolved dipole mapping under device operation condition, i.e. illumination, is lacking. Here, we map simultaneously the molecule dipole orientation pattern and the electrostatic potential with atomic resolution using light-illuminated cross-sectional scanning tunneling microscopy and spectroscopy.

Our experimental observations demonstrate that a photo-driven dipole reordering, initiated by a photo-excited separation of electron-hole pairs in spatially displaced orbitals, leads to a fundamental reshaping of the potential landscape in halide perovskites, creating separate one-dimensional transport channels for holes and electrons. We anticipate that analogous light-induced polarization order transitions occur in bulk and are at the origin of the extraordinary efficiencies of organometal halide perovskite-based solar cells as well as could reconcile apparently contradictory materials' properties.

3:05pm **PCSI-1WeA-14 First Principles Study on Electronic Properties of Graphene Nanostructures for High Current Density Cathode***, Nan Zhao, L Xu, M Lin,* Hanyang University, South Korea*; T Leung,* National Chung Cheng University, Republic of China*; H Hsu,* National Taipei University of Technology, Republic of China

Graphene is a crystalline allotrope of carbon with two-dimensional properties. Its carbon atoms are densely packed in a nano-scale hexagonal pattern. Graphene has many unusual properties. It is about 200 times stronger than the strongest steel. It can efficiently conduct heat and electricity and is nearly transparent. In this work, we study the electronic properties of graphene using first principles or *ab initio* calculations based on density functional theory (DFT) in order to explore its applications in field emission devices. The change of work function due to the lattice deformation of graphene is investigated using a supercell including a vacuum layer which is thick enough so that the layer interaction is negligible. It is found that the work function is very sensitive to the lattice size. As the lattice site increases, the work function increases proportionally. However, the work function is reduced doubly while the lattice site is reduced. The local work function of graphene has also been determined and this can be used to predict field emission current from Fowler-Nordheim equation more accurately. For realistic applications, this approach has been used to calculate the work function of carbon nanoribbons with different widths and terminating edges with and without passivation.

3:10pm **PCSI-1WeA-15 Band Offset Modulation in Si-EuO Heterostructures *via* Controlled Interface Formation***, W Li, A Posadas,* The University of Texas at Austin*; **Alex Demkov,*** The University of Texas

In a Si-based spintronic device, Si serves as the spin channel material. Owing to its small spin-orbit coupling, Si has a long spin relaxation lifetime and long spin coherence length, making it an excellent choice. Because the rock salt lattice of EuO is compatible with the ***fcc*** lattice of Si (see Fig. 1), and EuO is thermodynamically stable on Si, Si/EuO heterostructures have a real potential for use in Si-based spin-FETs. Combining first principles calculations and experiment, we investigate the atomic and electronic structure of the Si/EuO interface. We consider the thermodynamic stability of interface structures with different levels of oxidation to identify the most probable configuration. By comparing the calculated band alignment and core level shifts with measured values, we validate the theoretically constructed interface model. EuO has unusual electronic properties in that its charge neutrality level appears to be inside the conduction band [1,2]. In Fig. 2 we show a contour plot of the partial density of states (PDOS) as a function of energy and position along the *z* direction normal to the plane of the interface. In the contour plot one can clearly see the band edges of Si and EuO and read off the VBO, which is +0.19 eV. We find that the band offset can be tuned by altering the relative energy positions of the Si and EuO conduction bands via interface oxidation, which can be used to tune this materials system for specific applications in spintronics [3].

Figure 1. Top view of rock salt EuO and face centered silicon lattices. Purple ball represents Eu, red O and blue Si. It can be seen that rocksalt and face centered lattices match well. It can also be rotated by 45°.

Figure 2. Contour plot of PDOS for spin-up channel in the valence band and band gap regions. The dark blue region is the band gap and the yellow region is the valence band top.

[1] N. Jutong, I. Rungger, C. Schuster, U. Eckern, S. Sanvito, and U. Schwingenschlögl, Phys. Rev. B **86**, 205310 (2012).

[2] L. Gao, W. Guo, A. B. Posadas and A. A. Demkov, Phys. Rev. Materials **3**, 094403 (2019).

[3] W. Li, A. B. Posadas, and A. A. Demkov, *in press,* Phys. Rev. B (2019).

+ Author for correspondence: demkov@physics.utexas.edu

3:15pm **PCSI-1WeA-16 First Principles Study on Electronic Properties of Magnetite for Spin Polarized Emission under an Electric Field***, **Liang liang Xu,** N Zhao, M Lin,* Hanyang University, South Korea*; T Leung,* National Chung Cheng University, Republic of China*; H Hsu,* National Taipei University of Technology, Republic of China

Magnetite is a mineral and one of the main iron ores. With the chemical formula Fe_3O_4, it is one of the oxides of iron. Magnetite is the earliest discovered magnet, around 1500 B.C. It crystallizes in the inverse cubic spinel structure (Fd3m) above the so-called Verwey transition temperature, which is about 120 K. In this work, we study the electronic properties of magnetite (100), (110), and (111) surfaces under external electric fields using first principles or *ab initio* calculations based on density functional theory. With an electric field applied, the surface properties could be modified. For example, the (111) surface with an O_2 termination, the half-metal behavior becomes metal behavior under a critical electric field. With a +U calculation, most of the surfaces with different terminations show half-metallic, different from those predicted by a without +U calculation. We can use an electric field to control the metallic properties to be metallic or half-metallic. Un addition, the effective work function changes under different field strength. By calculating the local work function, we can know the distribution of work function on a certain surface. The effective work functions of magnetite Fe_3O_4 on different surfaces have been determined. The local work function has been found to have the correspondences with the atoms' positions and charge densities. It is proposed that the magnetite as a half-metal can possibly be used as a spin-polarized electron source.

3:20pm **PCSI-1WeA-17 Work Functions of Alkali and Alkaline Earth Metal Surfaces under Electric Fields based on First-Principles Calculations***, Y Wang, L Xu, **Ming-Chieh Lin,*** Hanyang University, South Korea*; T Leung,* National Chung Cheng University, Republic of China*; H Hsu,* National Taipei University of Technology, Republic of China

Alkali (Li, Na, K, Rb, Cs) and alkaline earth metal (Be, Mg, Ca, Sr, Ba) are widely used in various fields. In the field emission, the adsorption of alkali metals and alkaline earth metals to tungsten (W) will greatly change the work function. In this work, we study the work functions and local work functions of alkali and alkaline earth metal (100) (110) (111) surfaces under different electric fields using the first-principles or *ab initio* calculations. The convergence of density-functional-theory (DFT) calculations in the local-density approximation (LDA) and generalized-gradient approximation (GGA) with a plane-wave basis set the projector-augmented wave method as implemented in the Vienna ab-initio simulation package (VASP) has been carefully and systematically tested. For a comparison, the work functions have been calculated with five different pseudo potentials. By applying an electric field on the alkali and alkaline earth metals, we can calculate the effective work function, local work function and investigate the dependence of the effective work function and the local work function on the field strength.

[1] M. C. Lin, R. F. Jao, and W. C. Lin, J. Vac. Sci. Technol. B **26**, 821 (2008).

[2] T. C. Leung, C. L. Kao, and W. S. Su, Phys. Rev. B **68,** 195408 (2003)

[3] T. W. Pi, I. H. Hong, and C. P. Cheng, Phys. Rev. B **58**, 4149 (1998).

+ Author for correspondence: mclin@hanyang.ac.kr

Author Index

Bold page numbers indicate presenter