Electronic Materials and Processing
Room: 14 - Session EM+NS-FrM

Low-Resistance Contacts to Nanoelectronics
Moderator: S. Zollner, New Mexico State University

8:20am **EM+NS-FrM1 Electrical Transport on Chemically Modified Silicon-on-Insulator Substrates**, ***G.P. Lopinski***, National Research Council of Canada **INVITED**

Electrical transport of semiconductor surfaces and nanostructures are strongly influenced by interfacial processes. Adsorption and reaction events which result in charge re-distribution can modulate conductivity through long-range electric field effects. These effects are being exploited to tailor electronic properties of nanomaterials and devices as well as in the development of electrically-based chemical and biological sensors. Silicon-on-insulator(SOI) substrates, in which the top layer is thinner than the depletion length, are particularly well-suited for demonstrating and investigating the effects of surface processes on electrical transport. Measurements on hydrogen terminated H-SOI substrates (with both (100) and (111) orientations) have demonstrated that adsorption of certain polar molecules (water, pyridine and ammonia) results in large reversible increases in conductivity, attributed to charge transfer effects which induce accumulation of majority carriers on n-type and minority carrier channels (inversion) on p doped substrates. Adsorption of the prototypical electron acceptor tetracyanoethylene (TCNE) results in a strong decrease in conductivity on n-type substrates due to depletion of majority carriers. This effect is not fully reversible due to reactions of TCNE with the H-terminated surface. Use of SOI substrates also facilitates formation of point contact pseudo-MOSFETs, allowing transistor characteristics to be obtained without the need for device fabrication. This approach has been shown to be a simple and straightforward way to monitor the effect of adsorption and reactionevents on the electronic properties of the silicon substrate. Pseudo-MOSFET measurements have been used to monitor surface reactions such as ambient oxidation of the H-terminated surface. Gas phase photochemical reaction of alkenes has been used to chemically passivate these surfaces while maintaining a low density of electrically active defects ($<1x10^{11}$ cm^{-2}). These alkyl monolayer passivated SOI surfaces show a large reversible response to TCNE, suggesting they can function as good ultrathin gate dielectrics for sensing applications.

9:00am **EM+NS-FrM3 Evidence for Single Electron Tunnel Junction using Gold Nanoparticles on Oxide-Free Si(111)**, ***L. Caillard***, *O. Seitz, P. Campbell,* University of Texas at Dallas, *O. Pluchery,* Université Pierre et Marie Curie, France, *Y.J. Chabal*, University of Texas at Dallas

It has been suggested that the phenomenon of Coulomb blockade could be achieved by placing a metallic nanoparticle between two tunnel junctions. While the Coulomb blockade has been well established theoretically and demonstrated on metal substrates[1], it is more challenging to observe on semiconductor surfaces due in part to the defective nature of the interfaces and to the depletion layer. We present an experimental study of two ultra small-capacitance normal tunnel junctions connected in series between the Si substrate and a STM tip. To achieve such a structure, we use an amine-terminated self-assembled monolayer (SAM) grafted on silicon (111) as the insulator layer, acting as a linker to attach gold nanoparticles on the surface. The SAM layer is grafted directly on oxide-free silicon through a Si-C bond formation using hydrosilylation reactions and is characterized by a low interface state density[2]. Moreover, this SAM layer provides a long-term passivation (weeks) of the interface that prevents oxidation of the substrate during Au nanoparticle deposition. The SAM quality is characterized using an extensive range of techniques, including in-situ IR spectroscopy, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS) and Atomic force microscopy (AFM). The second capacitance is formed by the gap between the gold nanoparticle and the tip of the Scanning tunneling microscope/spectroscope (STM/S). The current-voltage measurements have been performed in ultra high vacuum. Several parameters have been investigated: silicon doping level, sample temperature, and size of the gold nanoparticles (AuNPs), ranging from 1 to 15 nm. The junction is achieved by either grafting synthesized AuNPs or depositing evaporated gold directly on the SAM. Preliminary data confirm that coulomb staircases are observed under different conditions, mostly clearly for highly doped substrates at low temperature (10K). The steps width and height of these Coulomb staircases depend on particle size. These results are an important step toward future control for single electron transistor and flash memory applications.

[1] Zhang, H.; Yasutake, Y.; Shichibu, Y.; Teranishi, T.; Majima, Y., Tunneling resistance of double-barrier tunneling structures with an alkanethiol-protected Au nanoparticle. *Phys. Rev. B*, 72, (20) (**2005**)

[2] D. Aureau, Y. Varin, K. Roodenko, O. Seitz, O. Pluchery and Y. J. Chabal, Controlled Deposition of Gold Nanoparticles on Well-Defined Organic Monolayer Grafted on Silicon Surfaces. . Phys. Chem. C, 114 (33), pp 14180–14186 (**2010**)

9:20am **EM+NS-FrM4 A Distribution of Variable Size Sn-islands on 0.8 nm Oxide/ Si (111): Local MOS Properties and Tunneling Studied with Synchrotron Radiation**, ***A. Silva***, Universidade Nova de Lisboa, Portugal, *K. Pedersen,* Aalborg University, Denmark, *Z.S. Li,* Aarhus University, Denmark, *P. Morgen*, University of Southern Denmark

The thinnest possible uniform and stable oxide layer grown thermally on Si (111) is 0.8 nm thick. This oxide is grown at around 500ºC, in a self-limiting process, which has earlier been fully characterized with surface sensitive, high-resolution core level photoemission at the ASTRID storage ring facility at Aarhus, Denmark. Such oxides are too thin for use in current generations of CMOS-devices, yet they have potential applications in devices, where controlled tunneling could be of importance, or as diffusion barriers. To study the tunneling properties of this oxide covering the Si (111) surface isolated nanometer-sized Sn islands in different diameters and concentrations were deposited at 500ºC and became negatively charged, with different charges depending on their size. The deposition was done from a Knudsen source in a way programmed to produce a systematic variation of the Sn coverage across about 2 cm of the surface. This is done to allow locally resolved photoemission characterization of the system, at a resolution (with a photon beam width) of around 150 micron. The resulting shifts of Si 2p and Sn 4d core levels at, and across the surface, with varying amounts of Sn, and charge on the Sn islands, are used to determine the local changes in band bending and fields in the oxide. This method thus offers a unique possibility to evaluate MOS properties of nano-systems in-situ without direct electrical contacts.

9:40am **EM+NS-FrM5 Signatures of Interface Band Structure and Parallel Momentum Conservation of Hot Electrons across Metal-Semiconductor Schottky Diodes**, *J. Garramone,* Northwestern University, *J. Abel, R. Balsano,* University at Albany-SUNY, *S. Barraza-Lopez,* University of Arkansas at Fayetteville, ***V.P. LaBella***, University at Albany-SUNY

Understanding hot electron transport and scattering through meterials and interfaces is important for conventional integrated circuit technologies and futuristic applications such as hot carrier photovoltaics and hydrogen sensing. In this presentation, the hot electron attenuation length of Ag is measured utilizing ballistic electron emission microscopy (BEEM) on nanoscale Schottky diodes for Si(001) and Si(111) substrates. Marked differences in the attenuation length are observed at biases near the Schottky barrier depending upon the substrate orientation, increasing by an order of magnitude only for Si(001), while remaining unchanged for Si(111). These results provide clear evidence that the crystallographic orientation of the semiconductor substrate and parallel momentum conservation affect the hot electron transport across these interfaces. A theoretical model reproduces the effect that combines a free-electron description within the metal with an ab-initio description of the electronic structure of the semiconductor.

10:00am **EM+NS-FrM6 Metal-Fullerene Interfaces: A Dynamic System**, ***P. Reinke***, *J.B. McClimon, H. Sahalov*, University of Virginia

Fullerenes and other small organic molecules are used in organic solar cells, organic LEDs and molecular electronics system, and the interface between the organic layer and the metal electrode is critical to achieve the desired functionality. The majority of studies focusses on the interaction of molecules with metal surface, and the interaction of metals with organic surfaces has garnered much less attention. However, the addition of metal to an organic layer surface has been one of the bottlenecks in the fabrication of molecular electronics devices. We therefore present here a comprehensive study of the metal interaction with fullerene surfaces. Our past research has investigated the deposition of Au and Si on fullerene surfaces, and our presentation here focuses on the interface to transition metals Vanadium and Tungsten. All of these systems show a dynamic behavior: the metal atoms are highly mobile and thus perturb the C_{60} matrix substantially.

The fullerene and metal atoms/films are deposited by electron beam and thermal evaporation, and the interface formation is observed with STM under UHV conditions in a sequential manner. V immediately diffuses into the fullerene matrix, and surface clusters are sparse. The STM images reflect the change in the local electronic structure of the molecules through

the interaction with sub-surface V: the apparent height of molecules in contact with V is reduced, and their rotation ceases and the molecular orbitals can be identified by the characteristic C_{60} substructure within the molecule.

We suggest that the subsurface V forms complexes with C_{60} where charge donation to the fullerene cage occurs, and preferential bonding to the hexagonal face determines the molecule orientation. The increase of V concentration leads to agglomeration of V-clusters and consequently the extension of regions with a smaller apparent height in the filled state images. The charge exchange between metal clusters and fullerene matrix allows to observe the V-cluster growth within the matrix. The empty state images are essentially flat, and show small variations in topography and cracks in the fullerene layer for large V-concentrations (~ 0.6 to 1 ML). We will present a comprehensive model for the diffusion of V through the matrix, the complex formation and cluster growth. The behavior of W is distinguished by a larger percentage of surface clusters, and the dynamics of cluster formation within the matrix will be compared to V. However, both transition metals do not destroy the C_{60} matrix, but only react to form carbides at elevated temperatures.

10:20am **EM+NS-FrM7 Scaling Silicide Contacts in Microlelectronics: At What Size will Material Characteristics affect Device Poperties ?**, ***C. Lavoie***, IBM T.J. Watson Research Center **INVITED**

With the continued scaling of CMOS technology, the typical contact area to the source and drain of a CMOS device can now reach below 1000 nm^2. At these nano-dimensions, typical intrinsic contact resistivities of $1x10^{-8}$ Ω-cm^2, easily lead to resistances exceeding the KΩ solely for crossing the interface silicide-silicon. Such resistances are unacceptable as they dominate the overall resistance of a device. In an attempt to mitigate this increase in interfacial resistance with contact area reduction, much research has been performed concentrating on the tailoring of material properties of both the silicide and the semiconductor substrate as well as on the optimization of contact geometries and the advanced engineering of interfaces.As the size of the contact reaches dimensions that are similar or smaller than the typical microstructure of the expected poly crystalline material, some dramatic effects are to be anticipated. First, the presence of a single grain during the silicidation eliminates the typical dominant diffusion path: grain boundaries. As a result, phase nucleation and kinetics of growth can only proceed through the silicide bulk or the available interfaces. This will likely retard formation of the desired phases in the narrowest dimensions. Another expected disadvantage of very small contacts resides in the variability of the intrinsic contact resistance discussed above. It is accepted that the Schottky barrier height of a given silicide to a silicon substrate varies with substrate orientation. As a result, variation of crystal orientation from contact to contact may lead to dramatic effects on contact resistance. This orientation variation can originate from either a variation in silicide texture from contact to contact or a variation in device geometry (i.e. silicidation on Si(100), Si(110) or Si nanowire device depending on geometry).In this presentation, we will first explain how the importance of contact resistivity has caused a shift in contact engineering from yield and defect control towards the optimization of device performance. We will then describe some of the challenges involved in building arrays of nanostructures and characterizing them.

11:00am **EM+NS-FrM9 Compositional Dependence of the Dielectric Function and Optical Conductivity of NiPt Alloy Thin Films**, ***L.S. Abdallah***, *T. Tawalbeh, I.V. Vasiliev, S. Zollner,* New Mexico State University*, C. Lavoie,* IBM T.J. Watson Research Center*, A. Ozcan,* IBM Systems and Technology Group*, M. Raymond*, GLOBALFOUNDRIES

Optical properties of metals are less well known than those of insulators and semiconductors, because it is hard to achieve similar purity and crystallinity in metals. Many metals are reactive and easily form oxides, or they exhibit significant surface roughness. We report the dielectric function and optical conductivity of Ni-Pt alloys as a function of composition (10 to 25 atomic % Pt) from 0.8 to 6.5 eV. Our films are 10 nm thick and were prepared by physical vapor deposition (co-sputtering from pure Ni and Pt targets). To avoid reaction between Si and the metal alloy, films were deposited on thick thermal oxides (220 nm). Some films were annealed at 500°C for 30 s. Similar Ni-Pt alloys are used as Ohmic contacts in CMOS device processing, to achieve highly stable low-resistance contacts between copper back-end metallization and front-end silicon transistors. Our results will enable in-line process control of Ni-Pt alloy deposition using spectroscopic ellipsometry.

Since our metal thickness is below the penetration depth, the interference from the thick SiO_2 layers creates artifacts when extracting the optical conductivity. We minimize this issue by acquiring the ellipsometric angles over a broad range of incidence angles (20° to 80°), which varies the optical path length and thus shifts the interference problems to different energies. Our resulting dielectric functions are similar to those tabulated by Palik for pure Ni. The data are dominated by a Drude divergence due to free carriers at low photon energies. We can remove this divergence by multiplying with the photon energy. We find several trends: (1) The optical conductivity of the annealed films is always greater than that of the as-deposited films, due to improvements in crystallinity and reduced grain boundary scattering after annealing. (2) All four alloys show conductivity peaks near 1.5 and 4 eV due to transitions from the d-like valence bands to the s-like conduction bands. (3) These peaks are significantly broader and weaker than those in pure Ni, but at the same energy. The broadenings increase with increasing Pt content. However, the amplitude of the 4 eV conductivity peak remains constant near 3500/Ωcm, independent of Pt content.

From electronic structure calculations for pure Ni and Pt and a Ni_3Pt ordered compound, we find that Ni, Pt, and Ni-Pt d-bands have similar energy, which explains why the 4 eV peak in the conductivity does not shift with Pt addition. Furthermore, the bandwidth of the Ni 3d bands is smaller than that of the Pt 5d bands, consistent with the increase in the broadening of the optical transitions.

This work was supported by NSF (DMR-11104934).

11:20am **EM+NS-FrM10 Ultra-Shallow Junction Formation for sub-22nm CMOS Technology and Characterization using High-resolution SIMS**, ***M.J.P. Hopstaken***, *H. Wildman, D. Pfeiffer,* IBM T.J. Watson Research Center, *Z. Zhu, P. Ronsheim,* IBM Systems and Technology Group*, K.K. Chan, I. Lauer, J.S. Newbury, D.-G. Park*, IBM T.J. Watson Research Center

Secondary Ion Mass Spectrometry (SIMS) has shown great resilience over the last decades in keeping up with the aggressive downscaling of advanced CMOS technology. Major improvements contributing to the staying power of SIMS are lower primary ion beam energies to meet the ever more stringent depth resolution demands [1] and application of novel external standard-free calibration methods for quantification in the near-surface region [2]. Here we demonstrate state-of the-art applications of SIMS to Ultra-Shallow Junction (USJ) formation and in-situ doped thin epitaxial layers.

We present As-USJ extension formation for nFET with junction depths below 120 Å, obtained using low energy ion implantation and micro-second flash (μ-flash) annealing. SIMS depth profiling employing a 200 eV Cs^+ beam provides detailed information on diffusion and segregation of As at the sub-nm scale for different annealing conditions. Low energy implantation of P has been proposed as an alternative to As for the formation of Source/Drain (S/D) regions to reduce crystalline damage. This is crucially important for advanced CMOS technology based on Extremely Thin SOI or FinFET. Here, we present different analytical approaches to determine the most accurate quantification for shallow P concentration profiles in Si. Also, we have employed 3D atom probe tomography to independently determine in-depth [P] profiles for SIMS calibration purposes [3].

For pFET processes, nm-scale control of B-diffusion is instrumental to obtain highly activated and abrupt B-USJ. Here we present a novel doping strategy employing ultra-thin solid source Si:B diffusion sources –in combination with μ-flash annealing– to form the B-USJ extensions. Presence of high [B] and minimal diffusion length necessitates use of ultra low O_2^+ impact energy for accurate determination of junction depth and abruptness. Regarding S/D formation, In-Situ Boron Doped (ISBD) SiGe is an important technology element for pFET strain enhancement. Quantitative analysis of [B] in SiGe using reactive low energy O_2^+ ion sputtering is complicated due to large yield variations as a function of [Ge] [4]. We present a calibration protocol based on multiple B-implanted epitaxial $Si_{1-x}Ge_x$ standards on Si(100) with constant [Ge] ranging from 20 to 50 at.%. This approach allows for explicit correction of both SiGe sputter yield and B^+ and Ge^+ yield variations as function of [Ge], enabling quantitative analysis of ISBD SiGe.

[1] A. Merkulov et al., JVST B **28**(1) (2010) C1C48.

[2] W. Vandervorst et al., AIP Conf. Proc. **931**(1) (2007) 233-245.

[3] M.J.P. Hopstaken *et al*, SIA, DOI 10.1002/sia.4916 (2012).

[4] Z. Zhu et al., SIA **43**(1-2) (2011) 657-660.

11:40am **EM+NS-FrM11 A Deep Dive into the Liquid Fermi Sea**, ***R.K. Schulze***, *J.C. Lashley, B. Mihaila, D.C. Wallace*, Los Alamos National Laboratory

We reexamine high resolution photoemission in some of the liquid metals accessible in a UHV environment. These include Ga, In, and Bi, and at a basic level, involves comparison of the DOS EDCs between the crystalline solid and liquid metal. The motivation is to gain an understanding of the fundamental differences between normal and anomalous melters. This includes a search for an understanding of the electronic contribution to the melt phase transformation. Normal melters, such as In, show a difference in liquid and crystal solid entropy at constant volume, $\Delta S^*=0.8\pm0.1$ k_b/atom, and exhibit a volume expansion upon melting, while anomalous melters,

such as Ga and Bi, have $\Delta S^{*}>>0.8\ k_b$/atom, and show a volume collapse upon melting. Observed changes to the electronic structure near the Fermi energy upon crossing the solid-liquid phase boundary will be discussed.

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