

Thursday Afternoon, November 2, 2017

Surface Science Division

Room: 25 - Session SS+AS+EM-ThA

Semiconductor Surfaces

Moderators: James Ohlhausen, Sandia National Laboratories, Petra Reinke, University of Virginia

2:20pm **SS+AS+EM-ThA1 Visualizing the Nanoscale Electrostatics of Material Interfaces, Vincent LaBella**, SUNY Polytechnic Institute, W. Nolting, University at Albany, SUNY **INVITED**

Electrostatic barriers at material interfaces are the foundation of electronic and optoelectronic devices. Their nanoscale uniformity is of paramount concern with the continued scaling of devices into the sub 10 nm length scale and the development of futuristic nanoscale devices. This creates a fundamental and technological need for nanoscale insight into the fluctuations of electrostatic barriers at material interfaces. This presentation will focus on our development of visualizing the nanoscale electrostatic fluctuations that are occurring at metal-semiconductor and metal-insulator-semiconductor interfaces. This is accomplished by acquiring tens of thousands of ballistic electron emission microscopy spectra on a grid and fitting them to get the local Schottky barrier height. Both false color images as well as histograms of barrier heights are then created and compared to theoretical modeling. This has given new insight into both the scattering of the hot electrons and the interface composition and their effect on the electrostatics. For example, interfaces with incomplete silicide formation and mixed metal-species interfaces have been imaged and when combined with cross-sectional TEM provide new insight into their effects on the electrostatics that is not possible with conventional bulk transport measurements or other metrology techniques.

3:20pm **SS+AS+EM-ThA4 Reactions of Benzoquinone with Hydrogen Terminated Silicon Surfaces, Meixi Chen, J.H. Hack, A. Iyer, R.L. Opila**, University of Delaware

Iodine and Quinhydrone(QHY) dissolved in methanol have long been known to react with hydrogen terminated silicon surfaces to passivate electronic defects where photo-excited carriers recombine non-radiatively. The mechanism of this passivation is not well understood. The two constituent parts p-benzoquinone(BQ) and hydroquinone(HQ) have been studied separately in this work. We have shown that even though BQ and HQ are a redox couple, they behave very differently in reacting with silicon surfaces. The reaction is photolysis, pH sensitive and solvent-dependent. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry were used to show that the BQ reacted with the surface. The electrical passivation of silicon surfaces is confirmed by carrier lifetime measurements where the silicon surface recombination velocity is decreased to 11cm/s. Changes in surface band bending are observed in XPS surface photovoltage. DFT calculations have also been performed. The reaction mechanism will be discussed in detail.

4:00pm **SS+AS+EM-ThA6 Uniform Reactivity and Bonding between Si(100) and GaAs(100) Wafers using Low Temperature (<180°C) Wet NanoBonding™ Optimized by Surface Energy Analysis, Nicole Herbots, R. Islam**, Cactus Materials

Bonding two semiconductor surfaces such as Si and GaAs can increase performance in solar cell efficiency and high power electronics. In this work, the surface chemistry and topography of Si and GaAs are investigated to optimize the bonding of the pair. A new process called Nano-bonding™ [1,2] can nucleate cross-bonding molecules via electron exchange between two surfaces into a macroscopically continuous bonding "inter-phase". The surfaces to be bonded are first chemically smoothed at the nano-scale and then terminated with matching "precursor phases". When activated, these phases exchange electrons. In other words, one surface is prepared so that it interacts preferentially with electron acceptors while the other surface is prepared to preferentially interact with electron donors. Hence, the precursor phases must be stable in air at room temperature until the surfaces are put into contact in clean-room class 10/ISO2 conditions and at low temperature (< 180°C). To bring the two surfaces into uniform contact while activating electron exchange and cross-bonding reactions, isotropic steam pressurization is applied, hence the name "Wet" Nano-Bonding™ [1,2].

The precursor phases are optimized based on insights provided by the Van Oss theory, combined with characterization of composition via Ion Beam Analysis (IBA), with surface energies via Three Liquids Contact Angle Analysis (3LCAA) and with surface topography using Atomic Force Microscopy. On smooth surfaces, the Van-Oss theory separates contributions to the total surface energy γ^T into molecular interactions γ^{LW} , and interactions

with electron donors γ^+ and acceptors γ^- . These can then be each extracted accurately from 3LCAA measurements [2] using multiple (>3) drops. NanoBonding™ is observed when surface pairs complement each other for electron exchange: one surface with high γ^+ and the other with high γ^- leads to the formation of molecular cross-bonds. However, IBA and 3LCAA characterization results show that this criteria is not sufficient. The total surface energies γ^T for both GaAs, and Si must be larger than 40 mJ/m². This is due to the fact that the contribution of interactions with electron donors and acceptors needs to amount to at least 10-15% of γ^T , so that total surface interaction γ^T is not mostly controlled by molecular interactions γ^{LW} , but exhibits significant non-molecular interactions with both acceptors and donors. Only then can the dominance of interactions with acceptors on one surface and interaction with donors on the other surface promote NanoBonding™ effectively.

[1] Herbots N. et al. US Patent 9,018,077 (2015); 9,589,801 (2017).

4:20pm **SS+AS+EM-ThA7 Evaluation of Silicon Oxidation in Downstream Plasma Photoresist Strip with Reducing Chemistries, Tongchuan Gao, V. Vaniapura**, Mattson Technology, Inc.

With the rapid development of ultra-shallow junction depth devices, minimized silicon surface damage with the photoresist (PR) strip processes is stringently required. Silicon oxidation associated with the strip processes results in silicon loss, and, therefore, adversely affects the source-to-drain current of the devices. This leads to an ongoing effort to develop strip processes with both high PR ash rate and low silicon oxidation rate. The commonly used PR removal technique, downstream oxidizing chemistry plasma, may result in significant silicon surface oxidation. Recently, reducing chemistry has been extensively investigated for PR stripping with very low silicon surface damage.

To understand the silicon oxidation behavior with PR removal using reducing chemistries, a series of experiments were conducted. Silicon wafers with controlled pre-processing native oxide thickness were treated in an inductively coupled plasma downstream reactor with different reducing chemistries. Processes with different reducing chemistry composition, plasma source power, processing time, and post-processing queuing time were systematically studied. Comparison was also made between reducing and oxidizing chemistries. The oxide growth was reduced by tuning the reducing chemistries as well as the hardware configuration. Ellipsometry and X-ray photoelectron spectroscopy (XPS) were used for oxide thickness measurement and quantitative chemical composition analysis for the pre- and post-processing wafers, respectively.

The experimental results demonstrated that higher H₂ content in the chemistry leads to more oxide growth, which may be attributed to that energized hydrogen species break the Si-Si bonds and then oxidation takes place, or that hydrogen can penetrate the silicon substrate and then be replaced by oxygen. Time-dependent oxidation tests showed that the oxide growth rate is higher for silicon wafers with thinner pre-processing native oxide layer due to the self-limiting nature of oxide growth. Most of the oxide growth happens within the first 30 seconds of the processes. PR ash rate and uniformity were monitored correspondingly to ensure satisfactory PR removal. Our work sheds light on the optimization of reducing chemistry plasma processes for efficient PR removal with minimal silicon oxidation.

4:40pm **SS+AS+EM-ThA8 Surface-sensitive Measurement of Dielectric Screening via Atom and Electron Manipulations, Daejin Eom, E. Seo, J.-Y. Koo**, Korea Research Institute of Standards and Science, Republic of Korea

Dielectric screening is essential in determining semiconductor properties. Its assessment on the surface, however, is beyond the capability of conventional capacitance and optical techniques due to their lack of surface sensitivity. Here we present the surface-sensitive measurement of the dielectric screening by using the scanning tunneling microscopy and spectroscopy. To be specific, we generate a single-atom defect on the surface and vary its ionization state by a single-electron charge. We then assess in-plane dielectric constant and Debye length at the surface by probing the surface potential modulation with atomic resolutions. Such single-atom and single-electron manipulations on B δ -doped Si(111) surface unravel that the dielectric screening on this surface is much in excess of what the classical image-charge model predicts, which we ascribe to the strained bonds and the ionic character of the surface layers. Also, as an exemplary application of the measured screening parameters, we demonstrate determining the ionization state of a surface defect from the defect-induced band bending.

5:00pm **SS+AS+EM-ThA9 The Effects of UV Irradiation, Stage Temperature, and Radical Flux on UV-Ozone Treatment using High-aspect-Ratio Cave Structures**, Shogo Uehara, T. Sugawara, P. Wood, SAMCO Inc.

UV-ozone treatment provides an atomic oxygen chemical reaction, where oxygen radicals are produced by UV-induced or thermal dissociation of ozone. Previously, it was found that ozone flux and stage temperature were critical for wettability improvement of polymer substrates such as polyetheretherketone (PEEK) [1]. However, in that study, the effects of UV irradiation, temperature, and oxygen radical flux were not clearly distinguished. In this research, a cave structure was employed to better elucidate the reaction mechanisms of UV irradiation, substrate temperature, and radical flux in UV-ozone treatment.

Polyimide-coated and photoresist-coated silicon coupons (5 mm x 5 mm) were placed at various depths inside a straight aluminum cave (6 mm x 6 mm square and 96 mm maximum depth). A SAMCO model UV-2 was used for this study. This system employs a cold cathode, mercury vapor UV lamp (185 nm and 254 nm), a remote (ex-situ) silent discharge high-concentration ozone generator (30-160 g/m³) and sample stage heating (50 to 200°C). The surface wettability of polyimide was examined using the water contact angle, and the photoresist ashing rate was measured using a stylus profilometer (Ambios Technology, XP-200).

Generally, samples placed at higher aspect ratios showed higher contact angles and lower ashing rates. This indicated that the reactive species were deactivated or did not reach the sample when the aspect ratio became larger (i.e. the depth of the sample in the cave became greater). At an aspect ratio of 15, with ex-situ ozone only (no UV irradiation) and a stage temperature of 100°C, the polyimide samples did not show a significant ashing rate or contact angle decrease. However, at 200°C, the samples processed with ex-situ ozone only (no UV irradiation) showed contact angle of 15.40° against the initial value of 93.70° and an ashing rate of 9.95 nm/min. The samples processed using UV irradiation with ex-situ ozone at 200°C showed a contact angle of 75.93° and an ashing rate of 7.67 nm/min.

From these results, it was concluded that production of oxygen radicals was accelerated by thermal dissociation of ozone at the higher temperature. The oxygen radical flux produced at high temperature gradually decreased in the cave as the aspect ratio became greater, but it remained relatively high and caused temperature-driven surface chemical reactions. It was postulated that the 254 nm UV irradiation dissociated ozone that otherwise would have reached deep inside the cave and thermally dissociated [2].

[1] Uehara, S., Kawabe, T., Wood, P., & Tsuji, O. (2016). *MRS Advances*, **1**.11, 743-748.

[2] Wood, P., Wydeven, T., & Tsuji, O. (1993). *MRS Proceedings*, **315**. 237.

5:20pm **SS+AS+EM-ThA10 Density Functional Theory Study of the Effects of Surface Defects on the Interactions of Cl and α -Fe₂O₃ (0001) Surface**, Qin Pang, H. DorMohammadi, O.B. Isgor, L. Árnadóttir, Oregon State University

Fe (III) oxides are the dominant structure of the outer layer of the iron passive film formed in alkaline environment, but chloride ions have been shown to induce depassivation of these passive films under the same conditions. Here we use hematite (α -Fe₂O₃) to represent the Fe (III) oxides and DFT+U method to investigate the mechanism of the depassivation by studying the interactions of Cl with both pristine α -Fe₂O₃ (0001) surface and the surface with defects. Total of four surfaces are considered, pristine surface, Fe vacancy surface, O vacancy surface and Fe-O pair vacancy surface. We found that the O vacancies have a positive effect on the adsorption of Cl on the surfaces while the Fe vacancy has a negative effect. The strength of the adsorption on the same site on the four surfaces can be ranked as O vacancy surface, Fe-O pair vacancy surface, pristine surface and Fe vacancy surface. The insertion of the Cl into the sub surface was studied on the four surfaces as well and was found to be endothermic for all four surfaces but surface defects have positive effects on the insertion of Cl by making it less endothermic. The insertion reaction is less endothermic on the O vacancy surface and Fe-O pair vacancy surface. On these two surfaces, the Cl insertion process goes through an O vacancy with reaction energy around 0.5 eV, which is about 1 eV lower than the reaction energy on the pristine surface. The Cl insertion energy is slightly coverage depended, but the insertion remains less favorable than the adsorption of Cl even at higher coverages.

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