

Electronic Materials and Photonics Division Room 101A - Session EM+AM+NS+PS-MoA

Atomic Layer Processing: Selective-Area Patterning (Assembly/Deposition/Etching)

Moderators: Michael Filler, Georgia Institute of Technology, Jessica Hilton, RHK Technology

1:20pm **EM+AM+NS+PS-MoA1 Area-Selective Deposition of Crystalline Perovskites**, *E. Lin, Brennan Coffey, Z. Zhang, P.Y. Chen, B. Edmondson, J.G. Ekerdt*, University of Texas at Austin

Epitaxial growth of crystalline perovskites enables opportunities in integrating perovskite properties into electronic and photonic devices. Pattern definition is a necessary step in many device applications and definition through etching can be problematic with titanium-based perovskites. We report a process to grow the perovskite film into the final patterned-dimensions through area-selective atomic layer deposition (ALD) followed by epitaxial regrowth from a crystalline substrate to form a single crystal perovskite film. Epitaxial barium titanate (BTO) films can be grown by ALD on strontium titanate (STO(001)) and STO(001)/Si(001) substrates. The substrates are coated with 40 nm of polystyrene (PS) and 185- and 264-nm UV light projected through a shadow mask is used to crosslink the PS under a N₂ atmosphere. The unexposed PS is stripped using toluene to expose the STO surface. Amorphous BTO films are deposited by ALD at 225 °C on the PS-patterned STO(001) surfaces. The low temperature process prevents the degradation of the PS layer. The PS mask is subsequently removed with an oxygen plasma exposure step. Atomic force microscopy and scanning electron microscopy after BTO growth and crosslinked-PS removal demonstrate high fidelity pattern transfer in the BTO films. Reflective high-energy electron diffraction and x-ray diffraction show that the film crystallizes after annealing the sample in vacuum at ≥ 750 °C, with oxygen partial pressure of 1×10^{-6} Torr. Film orientation as a function of annealing temperature is established with transmission electron and piezoresponse force microscopy.

1:40pm **EM+AM+NS+PS-MoA2 A Dry NF₃/NH₃ Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface**, *Christopher Ahles, J.Y. Choi*, University of California, San Diego; *A.C. Kummel*, University of California at San Diego

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination. The Siconi™ process is a dry clean which utilizes a low temperature (<30C) NF₃/NH₃ based plasma to selectively etch the native oxide layer on Si without etching the underlying Si layer. However the Siconi™ process leaves behind a (NH₄)₂SiF₆ salt which must be removed in a subsequent anneal. In this work we present a dry clean which eliminates (NH₄)₂SiF₆ salt formation and provides a surface which is just as flat as with the traditional aqueous HF clean.

The silicon surface following removal of the native oxide with an NF₃/NH₃ plasma was studied using X-Ray Photoelectron Spectroscopy (XPS) for elemental analysis as well as Atomic Force Microscopy (AFM) for surface roughness measurements. It was found that when the silicon substrate is held at 65-70C during the etching no (NH₄)₂SiF₆ salt formation is observed. The NF₃:NH₃ ratio was found to be a critical parameter for controlling the surface roughness, with the surface roughness decreasing with decreasing NF₃:NH₃ ratios. A NF₃:NH₃ ratio of 1:5 gave a Si surface with an RMS roughness of 3.4nm while a NF₃:NH₃ ratio of 1:10 gave a Si surface with an RMS roughness of 1.9nm. Further decreasing the NF₃:NH₃ ratio is expected to provide an even smoother surface, and experiments towards this end are ongoing. The plasma time was also optimized, and it was found that exposure to the NF₃/NH₃ plasma for 10 seconds and 1 minute resulted in essentially no removal of the native oxide, while exposure for 2 minutes resulted in complete removal of the native oxide. For comparison, Si surfaces cleaned with aqueous HF in our laboratory typically have ~10% oxygen and ~10% carbon contamination, while after cleaning with a NF₃/NH₃ plasma with NF₃:NH₃ = 1:10 for 2 minutes at 70C there was 3% O, 0% C, 4% F and 4% N impurities. Additionally, all of the silicon was in an oxidation state of 0 which means that there was no (NH₄)₂SiF₆ salt formation since this salt has silicon in an oxidation state of +4. To validate the applicability of this process, a molybdenum silicide film was deposited via atomic layer deposition (ALD) on dry-cleaned Si as well as on HF cleaned

Si. The RMS roughness of the ALD MoSi_x film on the dry-cleaned Si was 2.26nm while on the HF cleaned Si the RMS roughness was 2.78nm. This shows that the dry clean developed in this study is capable of producing cleaner and smoother Si surfaces than the traditional aqueous HF clean.

2:00pm **EM+AM+NS+PS-MoA3 Probing Strategies for Selective Deposition that Exploit Competitive Interactions**, *James Engstrom*, Cornell University
INVITED

Selective thin film processes, including atomic layer deposition, have the potential to enable next-generation manufacturing and patterning at the 5 nm node and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. Well-known for its ability to deposit atomically thin films with Å-scale precision along the growth direction and conformally over complex 3D substrates, atomic layer deposition (ALD) has emerged as a key nanomanufacturing process. In this regard, the range and scope of ALD-based applications and capabilities can be substantially extended by also controlling the in-plane growth—a timely and significant development that can be realized *via* area-selective deposition processes that depend on the chemical composition of the underlying surface. In this presentation we will review the approaches that have been taken to achieve area-selective ALD, and we shall highlight both the strengths and shortcomings of these approaches. We will also discuss our efforts to achieve selective deposition that exploit competitive interactions—these interactions can occur both on the surface(s) where the film is, or is not, being deposited, and in the gas phase. In our approach we couple well controlled experiments that involve *in situ* surface analysis using techniques such as X-ray photoelectron spectroscopy and high level quantum chemistry calculations of specific and non-specific binding of molecules to target surfaces. We find that this combination of techniques is capable of shedding considerable light on deposition processes that are both potentially fast and leave no trace of their use in guiding thin film deposition to those areas where growth is desired.

2:40pm **EM+AM+NS+PS-MoA5 The Interconnect Resistivity Bottleneck**, *Daniel Gall, T. Zhou, E. Milosevic*, Rensselaer Polytechnic Institute; *P.Y. Zheng*, Micron Technology

The effective resistivity of conventional Cu interconnect lines increases by more than two orders of magnitude as their width is decreased from 30 to 6 nm. The resulting increase in signal delay and energy consumption limits downscaling of integrated circuits. This presentation will discuss the search for the most conductive metal solutions for narrow interconnect lines, focusing on three key aspects. (i) Electron surface scattering: In situ transport measurements on epitaxial Cu(001) layers with various monolayer cap-layers demonstrate specular electron surface scattering when the local surface density of states at the Fermi level is negligible, resulting in a considerable copper resistivity reduction. (ii) Alternative metals: The resistivity scaling at reduced dimensions is measured using epitaxial metal layers (Cu, Ag, W, Ta, Ru, Mo, Ni) and directly compared to results from classical transport models using first-principles electronic structure calculations. Multiple elemental metals are expected to be more conductive than Cu for polycrystalline lines <10 nm. (iii) Confined transport model: First-principles non-equilibrium transport simulations in combination with measurements of the resistivity vs roughness and dimensionality are used to develop a new model that accurately accounts for electron surface scattering in quantum-confined 1-D and 2-D conductors. This model will replace semiclassical models that fail to predict the resistivity <10 nm.

3:00pm **EM+AM+NS+PS-MoA6 Sub 0.3 micrometer Copper Patterns Etched with a Plasma-Based Process and Pattern Dependent Electromigration Failure Mechanism**, *Yue Kuo*, Texas A&M University

Copper (Cu) is a popular interconnect material for high density ICs, large area TFT LCDs, and many advanced electronic and optical devices. Since Cu does not form volatile products under the conventional plasma etching condition, the only available method in preparing fine lines is the chemical mechanical polishing (CMP), i.e., the single or dual damascene, method. The author's group has invented a new plasma-based Cu etching method that has a high rate at room temperature (1). This method has been successfully demonstrated in defining submicron lines for IC chips as well as being used in the large area TFT LCDs (2). However, there are few papers on defining the sub 0.5 micrometer Cu line using this new etch method. The lifetime of the plasma-etch Cu line on the flat and stepped surfaces has been studied with the electromigration method (3,4). However, the pattern size effect is rarely discussed.

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In this talk, the author will discuss the process that can be used to prepare sub 0.3 micron dimension Cu patterns. The success of this process is due to the simultaneous Cu conversion reaction and sidewall passivation. In addition, the failure mechanism of the plasma-etched Cu line over a large range of line widths, i.e., from 1.5 to 30 micrometers, will be examined based on the electromigration test result. In summary, Cu lines prepared from the plasma-based process can be reliably applied in the many nano electronic and photonic products.

1. Y. Kuo and S. Lee, *Jpn. J. Appl. Phys.* **39**(3AB), L188-L190 (2000).
2. Y. Kuo, *Proc. 16th Intl. Workshop on Active-Matrix Flat Panel Displays and Devices*, 211-214 (2009).
3. G. Liu and Y. Kuo, *J. Electrochem. Soc.*, 156(6) H579-H584 (2009).
4. C.-C. Lin and Y. Kuo, *J. Vac. Sci. Technol. B*, 30(2), 021204-1 (2012).

3:40pm EM+AM+NS+PS-MoA8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials, Suzanne E. Mohnney, K.A. Cooley, M. Abraham, A.C. Domask, H. Simchi, L. Kerstetter, C. Lawrence, T.N. Walter, The Pennsylvania State University

INVITED

We review our recent studies of contacts to a variety of chalcogenide semiconductors, including few-layered molybdenum disulfide and tungsten diselenide, as well as the phase-change material germanium telluride. In some cases, diffusion of a transition metal into the semiconductor has been correlated with an especially low contact resistance. For example, annealing silver contacts on field effect transistors fabricated from few-layered molybdenum disulfide resulted in a reduction in contact resistance by a factor of 4–5 to 0.2–0.7 kOhm- μ m, while the ON/OFF current of the device remained high. Diffusion of silver into molybdenum disulfide was confirmed by secondary ion mass spectrometry. On the other hand, nickel appears to be even more soluble in molybdenum disulfide (as observed by Auger electron spectroscopy), but annealing nickel contacts resulted in an increase in resistance. For the phase-change material germanium telluride, incorporation of iron seems to play a role in achieving a low contact resistance of 0.004 Ohm-mm in annealed Au/Fe/Sn/p-GeTe contacts. Diffusion of iron into germanium telluride at a low but detectable level was found beneath a narrow-gap tin telluride interfacial reaction product using energy dispersive spectroscopy in the scanning transmission electron microscope. Using only iron or tin without the other did not result in such a low contact resistance. The influence of iron on the electronic properties of germanium telluride is now under study. Besides diffusion of metals into the semiconductor, we also present cases of reactive contacts to germanium telluride, whereby the contact resistance is greatly increased by interfacial reactions that led to the formation of a new phase (especially nickel tellurides and platinum tellurides). Finally, we consider the influence of surface diffusion on quasi van der Waals epitaxy of metals on layered transition metal dichalcogenides.

4:20pm EM+AM+NS+PS-MoA10 TiN_x and TaN_x Films via Low-T Thermal ALD using Anhydrous N₂H₄, Steven Wolf, M. Breeden, M. Kavrik, University of California at San Diego; D. Alvarez, J. Spiegelman, RASIRC; M. Naik, Applied Materials; A.C. Kummel, University of California at San Diego

For device back end of line processing, there is a need to deposit conformal barrier layers on high aspect ratio 3D architectures via low-T ALD. Titanium nitride (TiN) and tantalum nitride (TaN) have been studied as diffusion barriers to WF₆ during W metal fill and to Cu, as Cu can readily diffuse, causing device reliability issues. Organometallic-grown films are required when Cu is present to prevent etching, however, metal halide precursors are preferred for gate stack applications as films typically contain lower levels of carbon and oxygen contamination; this has been correlated with improved film conductivity. This work aims to deposit thermal ALD titanium nitride and tantalum nitride utilizing anhydrous N₂H₄ at lower temperatures than previously reported with NH₃ while still maintaining good film properties.

In this study, low temperature thermal ALD TiN_x from anhydrous N₂H₄ vs. NH₃ and TiCl₄ was performed on degreased and UHV annealed SiO₂/Si substrates at temperatures of 300°C and 400°C. The deposited films were studied using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). TaN_x films were grown at 150°C utilizing N₂H₄ and tris(diethylamido) (*tert*butylimido)tantalum (TBTDET) and characterized similarly. In addition, the resistance of air-exposed ultra-thin films was measured using a 4-point probe technique. Resistivities were estimated from thicknesses obtained from cross-sectional scanning electron microscopy (SEM) images. First, saturation dosing was performed to determine optimal half-cycle pulses of TiCl₄ and N₂H₄. After TiN_x ALD cycles,

AFM imaging showed uniform deposition with sub-nanometer RMS surface roughness. The corrected and normalized XPS showed near stoichiometric Ti₃N₄ with low O and C and ~10% Cl. There was approximately 2x more O and C and 50% more Cl in NH₃ grown films at 400°C. N₂H₄ films exhibited lower resistivities (359 vs. 555 μ ohm-cm), attributed to this lower contamination and likely better nucleation density. For TaN_x films, XPS of 15 cycles ALD TaN_x films resulted in 9% O and 4% C and had a Ta/N ratio of 4/5. Analysis on the Ta 4d peaks confirmed nucleation after the initial exposure of TBTDET (Si-O-Ta formation) based on the Ta 4d 5/2 peak BE of ~231.5 eV. A chemical shift to 229 eV was observed upon forming Ta-N bonds. Resistance measurements indicated insulating films consistent with the formation of Ta₃N₅. In summary, N₂H₄ grown TiN_x films showed lower resistivities with fewer impurities. The anhydrous N₂H₄ chemistry was extended to an organometallic Ta precursor, in which nearly stoichiometric films were deposited with low contamination at a modest substrate temperature of 150°C.

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