

Plasma Science and Technology Room 213A - Session PS1-WeM

Plasma in Nanoscale Applications

Moderator: W.M. Holber, MKS Instruments

8:40am PS1-WeM2 Growth, Characterization and Application of Plasma-Assisted Nano-Coatings, P.P. Joshi, R.V. Pulikollu, S. Higgins, S.M. Mukhopadhyay, Wright State University

Plasma-assisted coatings have significant application potential as they can be tailored to impart desired properties to the surface. The goal here is to develop a fundamental understanding of the initial stages of growth of these coatings on model flat substrates, and then test the applicability of these on uneven structures. Two types of plasma assisted functional coatings are studied: viz. oxide coatings that imparting surface reactivity (or hydrophilicity) and fluorocarbon coatings that imparting surface inertness (or hydrophobicity). XPS was used for detailed study of chemical composition of the substrate and coating atoms at various stages of deposition. Atomic force microscopy was used to study the morphology of these coatings as they grow. Combined XPS and AFM results for both the coatings rule out any possibility of the patchy coatings with exposed substrate (complete coverage of substrate), and also indicate that these coatings are effective on nanometer scale. These studies show that plasma-assisted chemical deposition can be a very viable approach to creating functional nano-coatings on surfaces of nano-structured solids. Initial studies on single-crystal silicon were followed up with comparative studies on different types of substrates (sapphire, graphite etc.). The effectiveness of these coatings on uneven surfaces such as composite core structures and fibrous films will be discussed.

9:00am PS1-WeM3 Plasmas Technologies in Microfluidics for Novel Bioanalytical Systems, T. Ichiki, Toyo University, Japan **INVITED**

Development of innovative nano-bio-analytical systems is coming to reality by the combination of the microfluidic device technologies and the precise image processing systems using an optical microscope or a scanning probe microscope. Highly functional microfluidic devices can be fabricated by the application of advanced nano/microfabrication technologies developed in the ULSI industry. Microfluidic devices under development in our projects are expected to enable direct manipulation and analysis of each single cell and obtain molecular-level information about life phenomena of the cell, which has not been attainable by the conventional analysis tools. Recent progress and the future scope in plasma processing for microfluidic devices will be presented in this paper.

9:40am PS1-WeM5 Fabrication of 7nm High Aspect Ratio Nanocolumns by Low Energy Neutral Beam Etching using Ferritin Iron-Core Mask, T. Baba, T. Kubota, Tohoku University, Japan; Y. Uraoka, T. Fuyuki, Nara Institute of Science and Technology, Japan; I. Yamashita, Matsushita Electric Industrial Co., Ltd., Japan; S. Samukawa, Tohoku University, Japan

The critical dimension of semiconductor devices is continuously expected to be decreased up to less than 50 nm within the next decade. However, the conventional lithography has a theoretical limit to define patterns smaller than wavelength of light. In this study, we report a new method to fabricate nanometer-scale structure by using biomaterial etching mask and a newly developed neutral beam etcher. A large number of atomically equal molecules can be easily produced due to the nature of biomaterials, such as proteins, that are synthesized based on the DNA information. Ferritin is a type of proteins, which is capable of biomineralization to make inorganic materials. It can biomineralize iron-core as hydrated iron oxide. By using the iron-core as an etching mask, we fabricated a number of 7nm nanocolumns in their diameters. Neutral beam etcher has been employed in this experiment. Neutral beams could realize accurate and damage-free etching because it could prevent charged particles and ultraviolet photons. Employing the uniform iron-core mask and neutral beam etching, high aspect ratio nanocolumn structure was successfully fabricated, and almost vertical sidewalls profiles were able to be achieved. The aspect ratio of 6.57 was achieved with 7 nm of the diameter, which was identical to that of the iron core. The neutral beam enabled damage-free etching and led to an accurate transfer from the iron-core to the silicon substrate without any aggregation of the iron-cores.

10:00am PS1-WeM6 Deposition of Nanocomposite Layers for Ultralow Dielectric Applications, G.R. Alcott, TNO-TPD, The Netherlands; M. Creatore, Eindhoven University of Technology, The Netherlands; J. Linden, TNO-TPD, The Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

As the dimensions of integrated circuit devices scale to smaller feature sizes, the resistance-capacitance (RC) delay of the metal interconnect will increasingly limit the performance of high speed logic chips. The integration of ultralow dielectric materials ($k < 2.5$) can reduce this problem and the use of the porous materials is now deemed necessary if the future targets of chip design are to be achieved [1]. While many candidates for ultralow-k applications exist, many of the most promising are synthesized using wet chemical processes involving harmful solvents and multiple process steps. In this work a novel dual plasma reactor is used to simultaneously synthesize and incorporate porous nanometre sized particles into $\text{SiO}_2/\text{C}/\text{H}/\text{ZrO}_2$ layers. Porous nanoparticles and siloxane layers are synthesized from a TEOS/O₂ and 1,2-bis(trimethyl)siloxymethane precursors respectively. Structure and composition of the nanocomposite layer produced are characterised using ESEM and infrared absorption spectroscopy. Thermal stability and electrical properties are determined to evaluate the thin films suitability in low-k dielectric applications. Dielectric constants as low as 1.82 ± 0.02 were achieved at 1 MHz. [FootnoteText@ footnote1@ http://public.itrs.net.

10:20am PS1-WeM7 Nano-Scale Pattern Transferring By Plasma Etching, Y. Zhang, C. Black, K. Guarini, T.J. Dalton, IBM T. J. Watson Research Center **INVITED**

Patterning challenges for the 22nm node and beyond in the ITRS roadmap requires precision etching of semiconductor nano-scale features at the sub-10nm regime. In this paper, we report the recent results of patterning true nano-scale features using plasma etching. A newly established method called "nanometer-scale pattern registration and alignment by directed diblock copolymer self assembly" was employed. Using this technique, large-scale (across 200 mm wafers) high-density ($> 10\text{E}6/\text{cm}^2$) nano-scale features were produced; both holes and line arrays with 40nm pitch were fabricated. These structures are beyond any state-of-art conventional optical lithography and e-beam writing technologies. The nanometer holes & line arrays were used to study plasma etching characteristics and challenges for different materials (silicon, silicon dioxide, and silicon nitride) with different plasma chemistries (fluorine-, chlorine-, and bromine-based). Besides scaling of the feature size or critical dimension, the thickness of the film stacks to be etched were also scaled. The patterning of nano-scale line arrays was more challenging than the patterning of nano-scale hole arrays when using ultra-thin and ultra-narrow diblock polymer masks. Among the challenges for line arrays were: (1) deformation of the polymer masks (due to poor thermal conductivity and film stress); (2) depth limitations due to selectivity to the mask; and (3) line edge roughness, (LER). These challenges have not only made the pattern transferring more difficult (even with current state-of-art plasma etching tools), but also indicate that plasma etching may be approaching a limits as it is currently implemented. A few proposed limiting factors of current etching tooling, underlying principles of different chemistries, and processing parameters and their advantage and drawback to etching nanometer scale features will also be discussed.

11:00am PS1-WeM9 Crucial Role of Side Wall Deposition during Synthesis of Spatially Separated Vertically Aligned Carbon Nanofibers by C-PECVD, A.V. Melechko, University of Tennessee, Knoxville; D.K. Hensley, Oak Ridge National Laboratory; X. Yang, K.L. Klein, University of Tennessee, Knoxville; H.M. Meyer, D.H. Lowndes, Oak Ridge National Laboratory; M.L. Simpson, Oak Ridge National Laboratory, University of Tennessee

Catalytic plasma enhanced chemical vapor deposition (C-PECVD) is used for deterministic synthesis of vertically aligned carbon nanofibers (VACNFs). In this process the location, orientation, diameter and length of the fiber can be controlled. Deterministic synthesis is extremely important for incorporation of nanofibers into devices with nanoscale elements such as microfabricated electron field emission sources, gene delivery arrays, intracellular electrochemical probes, scanning probe microscopy tips etc. In C-PECVD the formation of the carbon nanofiber via the catalytic particle is accompanied by the non-catalytic deposition of an amorphous carbon film over the surface. In order to prevent the undesirable film formation carbon source gas is diluted with etchant gases and the reactor is operated in an etching rather than deposition regime. The operating parameters usually are tuned so that the removal rate of carbon film is exactly equal to its deposition rate so that the growing nanofiber is not damaged. This is

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especially important for isolated nanofibers as their sidewalls are completely exposed. Such a balance is difficult to maintain over large-scale substrates with non-uniform patterns. We will report on a new regime in which Si from the substrate participates in the formation of a protective coating on the nanofiber sidewalls. In this process the formation of a carbon film is completely eliminated and the functionality of the VACNF is not affected. The results of SEM, EDX and AES with spatial resolution were used to determine the atomic composition and structure of coated carbon nanofibers. The dependence of side wall deposition on the plasma power, gas flow ratio and pressure will be discussed. In addition, a solution for non-silicon substrates will be offered.

11:20am PS1-WeM10 Catalytic Plasma Enhanced Chemical Vapor Deposition of Ultrasharp Vertically Aligned Silicon Nanocones and Their Characterization, K.L. Klein, A.V. Melechko, University of Tennessee/ORNL; P.D. Rack, University of Tennessee; D.K. Hensley, Oak Ridge National Lab; J.D. Fowlkes, University of Tennessee; H.M. Meyer III, L.F. Allard, D.H. Lowndes, Oak Ridge National Lab; M.L. Simpson, University of Tennessee/ORNL

We present a new method for the synthesis of vertically aligned ultrasharp silicon nanostructures with tip diameters as small as 10 nm. Silicon nanocones were produced using dc plasma-enhanced chemical vapor deposition (dc-PECVD) using the Si substrate as a sole source of Si and thin film Cu or Au as a catalyst. High resolution SEM, TEM, EDX, STEM, and AES were utilized to determine the microstructure and composition of the nanocones. We have explored variations in the structure and growth mode of these nanocones with respect to growth conditions. This structure will be described in detail and a growth mechanism proposed. The similarities and differences of this new growth process as compared to standard SiH₄-based VLS growth will be discussed. Finally, we will describe their potential use in applications such as gene delivery arrays and field emission cathodes.

11:40am PS1-WeM11 Gas-Phase Synthesis of Single-Walled Carbon Nanotubes by Hot-Filament-Assisted Plasma Chemical Vapor Deposition and Its Analysis by Mass Spectroscopy, Y. Hayashi, Y. Morimoto, Y. Kogawara, S. Nishino, Kyoto Institute of Technology, Japan

Single-Walled Carbon Nanotubes (SWNTs) have been successfully synthesized in gas phase by Hot-Filament-Assisted Plasma Chemical Vapor Deposition. Hot filaments were used for heating a reaction zone and for the assistance of generation and stabilization of DC plasma. Ethylene diluted 30 % in hydrogen was flowed through a pipe into a stainless chamber to the direction of the hot filaments. The vapor of ferrocene was included into the reaction gas before introduction to the chamber. Three tungsten wires were stretched and they were heated 1800-2000 °C. The pressure in the chamber was maintained 3.33 kPa (25 Torr). At 25 mm downstream of gas flow from the hot filaments, a copper plate was placed perpendicular to the flow. DC voltage of +300 V with the current of 150 mA was applied to the copper plate with the hot filaments and the chamber grounded. Glow discharge plasma was generated between the hot filaments and the copper plate for about one hour. Carbon fine particles collected on the plate as well as on another plate put under the plasma on the bottom of the chamber were evaluated by Raman spectroscopy and they were confirmed to be SWNTs. The diameter of the SWNTs were observed by transmission electron microscopy to be 1 to 2 nm. The fact that more SWNTs were obtained on the bottom plate than on the downstream plate suggests their synthesis in gas phase. Quadrupole mass spectrometry was carried out for the analysis of molecules during the synthesis. The evolution of partial pressure of benzene corresponded well with the evaporation of ferrocene while that of iron did not. The results support that iron clusters were formed in gas phase through the decomposition of ferrocene and that large amount of SWNTs were grown on them being suspended in the glow discharge plasma for a long time.

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