Plasma Science and Technology Division
Room 23 - Session PS+AS-MoM

Plasma Processing of Challenging Materials

Moderators: Erik V. Johnson, LPICM, Ecole Polytechnique, France, Osamu Sakai, The University of Shiga Prefecture

8:20am **PS+AS-MoM-1 Control of Plasma Doping Conformality in FinFET Arrays**, ***Mona Ebrish***, *O Gluschenkov,* IBM Research Division; *M Hopstaken,* IBM T.J. Watson Research Center; *F Torregrosa,* Ion Beam Services

FinFET devices are rapidly emerging as a standard transistor architecture for extending CMOS scaling beyond the 22 nm technology node because of superior electrostatic channel control. One practical challenge is to achieve a high degree of conformality for source/drain (S/D) extension doping along the Fin sidewalls. Conformal extension doping is crucial to minimize finFET series resistance while maintaining electrostatic channel control. Precise control of transistor characteristics over large-scale CMOS circuits and systems mandates that the extension doping and its conformality be maintained over arrays of finFETs with tight fin pitch. Plasma doping, with its wide distribution of impinging ion angles, provides an alternative to conventional ion beam implantation for fin array sidewalls. The traditional 1D Secondary Ion Mass Spectrometry (SIMS) depth profiling technique is unable to quantify the doping profiles in fin array sidewalls and hence the 1.5D SIMS approach (SIMS through array of fins) is used in this study. The retained sidewall dose measured by 1.5D SIMS is compared to a predicted number of impinging plasma ions that arrive to the fin array with certain angle and energy distributions dependent on the plasma conditions. This comparison takes into account the impinging ion cut off angle caused by adjacent fin shadowing in tight-pitch arrays. Based on those findings, a tuning of the plasma conditions was applied to obtain better than 50% dopant uniformity along the Fin sidewalls. The ability to control impinging ion angle distributions in plasma doping provides a valuable tool for improving doping conformality in tight-pitch fin arrays.

8:40am **PS+AS-MoM-2 Study of Plasma-etching Parameter Impacts on Two-dimensional Electron Gas Degradation in AlGaN/GaN Heterostructures**, ***Frédéric Le Roux***, *P Burtin, N Possémé, A Torres, S Barnola,* CEA-Leti, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructrures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors and diodes.

Today, plasma-etching are considered as one of the most critical step in fabrication of such devices. Indeed plasma etching can lead to charge generation (depleting the channel)[1,2], AlGaN amorphisation (modifying the structure and the polarisations of the AlGaN)[3,4] or element implantation inducing charges or traps[5].

In this study, we propose to evaluate the impact of several plasma parameters (chemical, physical and physico-chemical) on 2DEG degradation occurring during silicon nitride etching (selectively to AlGaN). Experiments have been carried out on 200mm wafers using the following stack: 10nm Si_3N_4/24nm $Al_{0,22}Ga_{0,78}N$/AlN spacer/2µm GaN/buffer layers. The AlGaN degradation has been determine thanks to Rsheet and Hall measurements.

First the impact of a conventional fluorocarbon etch chemistry ($CF_4/CH_2F_2/O_2$/He) on 2DEG degradation will be presented as an ion-energy function. It will be demonstrated that Rsheet is degraded with the ion energy increase and confirmed by the evolution of career- density and mobility.

Then the pure-chemical etching effects (using wet and downstream-plasma etching process) as well as physical etching effects, with ion bombardment, (using Ion Beam Etching process (IBE)) will be discussed in term of Rsheet.

Finally, the benefit of new silicon nitride etching process, which has already been tested and validated for silicon nitride spacer application[6], has been evaluated for diode contact application. This process is based on two steps. In a first step, the film is modified in volume by a He plasma performed in a conventional etch tool (ICP) followed by a second step of selective removal (HF dip) of the modified layer (Si_3N_4) with respect to the non-modified material (AlGaN).

Thanks to this study, the plasma-etching's role in the channel characteristics degradation have been highlighted and linked to the plasma parameter through the Rsheet and Hall measurement evolutions. In order to increase the degradation mechanism understanding engendered by etching steps, physico-chemical characterisations will be developed to determine the degradation sources.

1. Cao, X. A. *et al.Appl. Phys. Lett.***75,** 2569–2571 (1999).

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3. Cao, X. A. *et al.Appl. Phys. Lett.***75,** 232–234 (1999).

4. Haberer, E. D. *et al.Appl. Phys. Lett.***76,** 3941–3943 (2000).

5. Cai, Y. *et al.Ieee Trans. Electron Devices***53,** 2207–2215 (2006).

6. Posseme, N. *et al. Appl. Phys. Lett.***105,** (2014).

9:00am **PS+AS-MoM-3 Spatiotemporal Non-uniformity of CVD Plasmas and Film Qualities**, ***Masaharu Shiratani***, Kyushu University, Japan **INVITED**

Here we discuss great impact of nanoparticles formed in CVD plasma on uniformity of the plasma and film qualities [1-5]. Uniformity of thickness, composition, structure, and properties is a major concern of plasma CVD films. Multiple precursors including radicals, ions, and nanoparticles contribute to the film formation and hence their flux and flux ratio to the surface determine the film uniformity. Although most studies and text books describe film formation due to radicals and ions, such precursors are predominant only for very low pressure (< 5 Pa); in a pressure range of 10-500 Pa for most plasma CVD, contribution of nanoparticles to the film volume is 10-60% and cannot be disregarded [1-3]. CVD plasma tends to have inherently spatiotemporal non-uniformity of its internal parameters mainly because of nanoparticles. Nanoparticles have long time constant of their nucleation and growth. They tend to be charged negatively and are trapped in plasma. Nanoparticles act as loss sites of electrons, ions, radicals, and nanoparticles; and hence they have great influence on non-uniformity of plasma parameters, deposition rate, and film qualities. Particularly, they tend to give nonlinear response of CVD plasma, such as hysteresis, to discharge power and pressure. We show a model which reproduces well such non-linear response, and contribution of nanoparticles is one of keys to realize uniformity of high quality films [4, 5]. There is plenty of room to improve qualities of plasma CVD films by paying attention to contribution of nanoparticles to the films.

Work partly supported by JSPS KAKENHI grant numbers 26246036 and 16K13922.

[1] K. Koga, et al., J. Phys. D, 40, 2267 (2007).

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[5] S. Toko, et al., Suf. Coat. Technol., (2017) doi.org/10.1016/j.surfcoat.2017.01.034.

9:40am **PS+AS-MoM-5 Surface-driven CH_4 generation from CO_2 in Low-pressure Non-thermal Plasma**, ***Kazunori Koga***, *S Toko, S Tanida, M Shiratani,* Kyushu University, Japan

The methanation of CO_2 attracts attention as the way to produce rocket propellant fuels at Mars because CO_2 comprises 95% of the atmosphere of Mars and water exists on Mars [1]. This reaction is called the Sabatier process and has been studied using catalysts under high pressure over 1 atm and high temperature above 200 °C to realize a high conversion efficiency. However, the pressure on Mars is 135 times smaller than that of the Earth, and the average temperature is extremely low of -63 °C [2]. A method using low-pressure non-thermal plasma allows methanation under low pressure and low temperature conditions [3]. Therefore, the plasma process is suitable for methanation at Mars. Here, we converted CO_2 to CH_4 using a capacitively coupled plasma (CCP) together with Cu catalyst. Experiments were carried out using a CCP reactor, excited at a frequency of 60 MHz. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The electrode material was Cu. CO_2 gas flow rate was 1.0 sccm and that of H_2 was 6.0 sccm . The pressure was 750 Pa and the temperature was room temperature. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. CH_4 yield depends on surface condition of Cu electrodes, indicating that surface reactions on Cu electrodes dominate the CH_4 generation. Moreover, CH_4 generation has a long time constant more than 500 s, whereas CO_2 conversion has a short time constant of 80 s. These results indicate that CO_2 conversion takes place in gas phase by electron impact dissociation, while CH_4 generation involves several reaction steps. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

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[2] M. Kano, G. Satoh, and S. Iizuka, Plasma Chem. Plasma Process **32**, 177 (2012).

[3] S. Toko, et al., Sci. Adv. Mater. In press.

10:00am **PS+AS-MoM-6 Plasma Modification of Carbon Fibres for Tough Carbon Fibre Composites***, **Sally McArthur**, R Radjef, B Fox,* Swinburne University of Technology, Australia

Carbon-fibre manufacturing is a well established process that includes a surface treatment and a sizing step which are fast and easily incorporated into the production process. In the electrolytic oxidation steps, ammonium bicarbonate is used to introduce functional and polar groups to the surface while weakly bound basal planes are removed and the surface roughness is increased. All these are desired effects that are then covered with the application of the sizing layer, which protects the fibre surface during subsequent processing steps. The size is generally an epoxy based emulsion that provides handleability, lubrication, protection and is supposed to create a strong bond. This production process creates a complex multilayered interphase that is not well understood. It is believed that the size partially reacts with the surface functional groups, leaving a sizing layer that is depleted in epoxide groups and hence not able to fully cure. Furthermore how do we know that enough hardener diffuses through the matrix to the fibre surface to fully cure the sizing layer in the first place?

The aim of this study is to replace the current surface treatment and sizing step by a two-step plasma approach that allows the formation of a controlled interphase. In part one of this project a comparative study between electrolytic oxidation and air plasma treatment has been performed. In a second stage plasma polymerisation of TMDSO was used to produce films of variable mechanical properties by controlling the plasma power. This talk will focus on the the development and characterisation of the lab-based plasma system used to deposit uniform coatings onto the carbon fibres using a reel-to reel process and dual electrode array.

10:40am **PS+AS-MoM-8 Damage Free Plasma Etching Processes of III-V Semiconductors for Microelectronic and Photonic Applications***, **Erwine Pargon**, M Bizouerne, C Petit-Etienne, L Vallier, G Gay, M Fahed, K Rovayaz, M Fouchier, C Bellegarde, V Renaud, G Cunge, O Joubert,* CNRS-LTM, Université Grenoble Alpes, France*; E Martinez, N Rochat,* CEA-Leti, France **INVITED**

Due to their inherent advantages of direct bandgap and high electron mobility, III-V semiconductor materials are today widely used as active materials for a wide range of applications including high-speed and power electronic devices, and many types of opto-electronic and photonic devices. Recent progress in both molecular wafer bonding technology and monolithic heteroepitaxy let envisage the integration of III-V semiconductors directly on a Silicon platform. If successful, such integration paves the way for the emergence of highly performant devices, taking advantages of both III-V unique properties and the maturity of Si processing. Some promising examples are the use of high mobility III–V channel materials to extend the performance of Si CMOS, or the unification of electronics and photonics by combining photonic components with a silicon platform for next-generation optical interconnects. For all these future technologies, development of industrial processes for III-V semiconductors patterning is necessary. Plasma etching allows feature patterning with a nanometric control of the dimension, but one major drawback is the creation of defects in the vicinity of the etched surfaces, that can change the electro-optical properties of the semiconductor, and ultimately compromise the device performance. There is today a lack of knowledge on by which mechanisms and to what extent the plasma etching process induces damage at the III-V pattern sidewalls and the consequence it has on the device performance. The objective of this work is first to provide a better understanding of plasma-induced damage at the sidewalls of micro-nano-patterned III-V semiconductors by establishing a direct link between structural and chemical modifications induced by plasma etching, and opto-electrical properties. Based on such comprehensive know-how, the second objective is to provide technological solutions to minimize this damage in order to propose low damage plasma process compatible with the fabrication of commercial devices. The present study mainly focuses on the plasma etching process development of InGaAs used as a high mobility channel in a FinFET for microelectronic applications and of InGaAs/InP heterostructures used as a laser in hybrid photonic integrated circuits. Etching experiments are carried out in industrial ICP reactors. The structural damage induced at the pattern sidewalls (amorphization, stoichiometry, roughness..) are evaluated by electronic microscopies, AFM and nanoauger spectroscopy. The optical properties of the III-V semiconductors at the pattern sidewalls are analyzed by cathodoluminescence.

11:20am **PS+AS-MoM-10 Fabrication of Metal Nanoparticle-dispersed Nanocomposite Films by *In Situ* Plasma Reduction of Metal Cation-containing Polymer Films***, D Boris,* Naval Research Laboratory*; **Souvik Ghosh**,* Case Western Reserve University*; S Hernandez,* Naval Research Laboratory*; C Zorman,* Case Western Reserve University*; S Walton,* Naval Research Laboratory*; M Sankaran,* Case Western Reserve University

Nanocomposites composed of inorganic nanoparticles and polymers have broad applications because of their unique combination of optical, electrical, thermal, and mechanical properties. A key fabrication challenge is dispersion of the two different phases which leads to separation and particle agglomeration. Compared to mixing premade nanoparticles with polymers, *in situ* formation of nanoparticles from a thin film containing the metal precursor and polymer has the potential to improve dispersion. Various approaches to reacting the metal precursor have been explored including heat treatment, UV exposure, and chemical processing. Low-temperature plasmas are particularly unique due to their inherent compatibility with temperature-sensitive polymers, and potential for rapid large-area processing. However, the mechanism for plasma-driven particle formation remains poorly understood.

Here, we carry out a systematic study of *in situ* plasma reduction of metal-cation containing polymer films to form nanoparticle-dispersed nanocomposites. Films were prepared from solutions of silver nitrate ($AgNO_3$) and polyacrylic acid (PAA). Chelation of the polymer with the metal cation produced a precipitate that was collected by centrifugation and cast as a thin film. The films were then exposed to a low-pressure, electron-beam generated plasma operating over a broad set of conditions aimed at delivering a controlled flux of low-energy argon ions. The as-treated films were analyzed with UV-visible absorbance spectroscopy and scanning electron microscopy (SEM). Absorbance confirms the presence of the localized surface plasmon resonance (LSPR) for Ag nanoparticles. The spectra show significant changes in the peak intensities with negligible shifts in the peak wavelength with plasma process changes, indicating that the particle concentration increases or decreases with a relatively constant average particle size. We correlated these changes in particle concentration to the variation in charge fluence at the film surface.

This work is partially supported by the Naval Research Laboratory base program and the National Science Foundation under Grant No. SNM-1246715.

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