

Atomic Layer Etching

Room Grand Ballroom A-C - Session ALE2-WeM

Plasma and Energy-Enhanced ALE

Moderator: Prof. Dr. Heeyeop Chae, Sungkyunkwan University (SKKU)

10:45am ALE2-WeM-12 Isotropic Plasma-Thermal Atomic Layer Etching of Aluminum Nitride Using SF₆ Plasma and Al(CH₃)₃, *Austin Minnich*, Caltech INVITED

We report the isotropic plasma atomic layer etching (ALE) of aluminum nitride using sequential exposures of SF₆ plasma and trimethylaluminum (Al(CH₃)₃, TMA). ALE was observed at temperatures greater than 200 C, with a maximum etch rate of 1.9 Å/cycle observed at 300C as measured using ex-situ ellipsometry. After ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a ~35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and wide bandgap semiconductor devices. [arXiv:2209.00150]

11:15am ALE2-WeM-14 GaN Atomic Layer Etching Using SF₆ and Ar Plasmas Controlled by RFEA and Langmuir Probe Measurements, *Remi Dussart*, Université d'Orléans - CNRS, France; *L. Hamraoui, T. Zhang, A. Crespi*, Université d'Orléans, France; *M. Boufnichel*, STMicroelectronics, France; *P. Lefaucheur*, CNRS, France; *T. Tillocher*, Université d'Orléans, France

Chlorine based plasmas are usually preferred to etch GaN because of the formation of GaCl₃ molecules at the surface, which are quite volatile¹. In fluorine-based plasmas, GaF₃ molecules are formed at the surface as well, but they are not volatile except at a very high temperature¹. However, in atomic layer etching, SF₆ plasma can be used to control the etching at the atomic scale. Indeed, the Ga surface can be saturated of fluorine, producing a monolayer of GaF_x sites, which are supposed to not desorb during the modification step. Then, this modified layer can be sputtered selectively during the argon plasma removal step if the sputtering threshold of this layer is lower than that of GaN.

In this presentation, we would like to highlight the advantage of using probes such as ion Retarding Field Energy Analyzer (RFEA) and Langmuir probes to control the ALE process. With such plasma diagnostics, it is possible to evaluate the energy of the ions bombarding the surface and adjust the process parameters in order to avoid direct sputtering of GaN, and selectively remove the modified layer.

We used an Inductively Coupled Plasma (ICP) reactor excited at a frequency of 13.56 MHz with an RF generator to perform the experiments. The self-bias voltage was varied using an independent RF power supply operating at the same frequency. Experiments were performed at different source powers and different pressures of argon. This study led to an optimized etching process, which enables the control of the etching at the atomic scale, monolayer by monolayer. An energy scan was carried out and the synergy of the ALE process was evaluated. In certain ion flux conditions during the removal step with the Ar plasma, a self-limiting regime could be obtained.

In parallel, we used and adapted the global model developed by Pascal Chabert's team² at the "Laboratoire de Physique des Plasmas" in Palaiseau, France, to our reactor in order to simulate the plasma parameters for both Ar and SF₆ plasmas under different experimental conditions. Finally, some material characterization experiments (AFM, XPS, and ToF SIMS) were performed to analyze the GaN surface after the ALE process.

Acknowledgment

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¹ S.J. Pearton, J.C. Zolper, R.J. Shul, and F. Ren, *J. Appl. Phys.* **86**, 1 (1999).

² C. Lazzaroni, K. Baba, M. Nikravech, and P. Chabert, *J. Phys. Appl. Phys.* **45**, 485207 (2012).

11:30am ALE2-WeM-15 Speedy and Smooth Atomic Layer Etching for Silicon Carbide with DC Bias-Pulsing, *Julian Michaels*, University of Illinois at Urbana-Champaign; *N. Deegan*, Argonne National Laboratory, USA; *Y. Tsaturyan*, University of Chicago; *R. Renzas*, Oxford Instruments; *D. Awschalom*, University of Chicago; *G. Eden*, University of Illinois at Urbana-Champaign; *J. Heremans*, Argonne National Laboratory

Atomic layer etching (ALE) is a cyclical process that shows promise for precisely fabricating nanostructures in a variety of materials. Silicon carbide (SiC) is a wide bandgap semiconductor material known for its excellent electrical, thermal, and mechanical properties. These properties make SiC a common material for power electronics, optoelectronics, and quantum optics. Conventional dry etching techniques for SiC suffer from poor selectivity, roughness, and damage the crystalline structure. ALE offers a solution to these shortcomings by utilizing self-limiting chemical reactions to remove individual atomic layers of SiC, resulting in precise etching that leaves smooth surfaces.

We present a novel execution of ALE for SiC using a bias-pulsing scheme and demonstrate self-limiting single dimer (i.e. the Si-C doublet) removal with an Ar/Cl₂ inductively coupled plasma reactive ion etching (ICP RIE) system by only pulsing the plasma DC bias. Gases are not purged between etch steps, which leads to etch cycles of merely 6 seconds, which are far shorter than those of conventional ALE methods. Our results show that this ALE process can achieve precise etching with sub-angstrom surface roughness. We believe that this technique will enable new SiC-based quantum devices, especially those that are sensitive to surface quality, and that bias-pulsed ALE can be applied to other material systems to provide a more rapid solution for ALE.

11:45am ALE2-WeM-16 Thermal Atomic Layer Etching of MoS₂ Films, *J. Soares, John Hues*, Micron School of Material Science and Engineering, Boise State University; *A. Mane, D. Choudhury, S. Letourneau*, Applied Materials Division, Argonne National Laboratory; *S. Hues*, Micron School of Material Science and Engineering, Boise State University; *J. Elam*, Applied Materials Division, Argonne National Laboratory; *E. Graugnard*, Micron School of Material Science and Engineering, Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS₂) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS₂ has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS₂ using MoF₆ and H₂O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS₂ films. In situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF₆ + H₂S) to the proposed etching chemistry (MoF₆ + H₂O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS₂ films once annealed. With the many application of both amorphous and crystalline MoS₂, this work helps to identify and expand current atomic layer processing chemistries.

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