Atomic layer etching: introduction and first uses

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Abstract

Atomic layer etching (ALE) is a cyclical etch process, mirroring the atomic layer deposition (ALD) process, but removing material. Like ALD, it had been known at least 20 years before it began to find applications. It is a slow process, and is likely to find its first uses where existing etch processes are deficient, such as in etching atomically thin heterostructures.

Introduction

Plasma etching converts solid material to gas by means of fluxes of chemical radicals and energetic positive ions. Plasma ALE separates the two fluxes in time: first a chemical gas dose is delivered, and later ion bombardment acts on adsorbed material, removing both the adsorbed species and some bound components of the solid surface. Additional time is normally required to clear gas phase chemical species before the etch phase, and possibly to clear reaction products before the next dose. Ideally both the dose and etch phases are self-limiting: the adsorbed layer forms a defined reservoir of reactant, and the etch step should be selective between bound species and the underlying solid matrix.

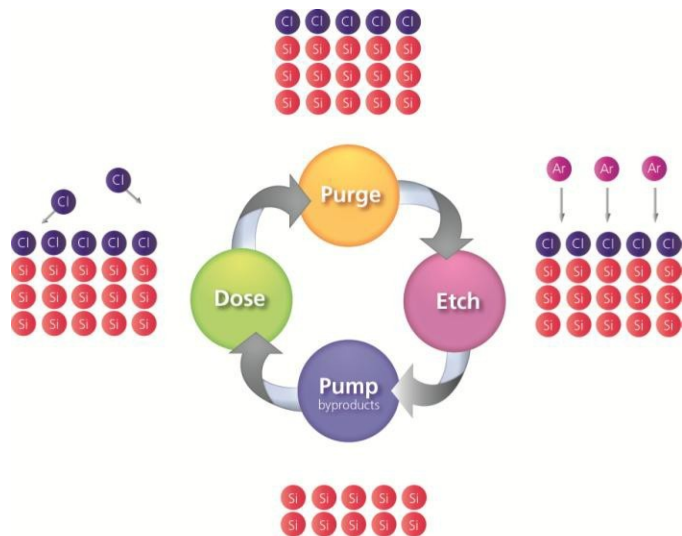

Figure 1: An ideal atomic layer etch cycle. A chemical dose is adsorbed (left); excess gas is removed (top); ion bombardment removes just the chemically bound species (right); reaction products are pumped away (left). The etching of silicon with chlorine under argon ion bombardment is depicted.

Plasma ALE of silicon was shown by Athavale and Economou in 1996 [1]. Other materials etched by ALE include GaAs [2], SiO_2 [3] graphene [4] and copper [5]. A purely chemical approach in the gas phase came later, notably through the work of Steven George's group [6] - differing from ALD, where thermal processes preceded plasma ALD. Wet ALE processes exist [7], and studies have also used ion or neutral beams for the etch step, rather than plasma [8].

Equipment

A plasma etcher with separate control of plasma generation and ion bombardment energy is required. Some of the chemical dose steps require radical creation either for a faster reaction (atomic chlorine saturating the surface faster than chlorine gas), or because the source gas does not itself bind to the surface (for example, CHF_3 used in ALE of silicon dioxide). Ion bombardment energy should be held below the threshold for etching in the chemical dose step, so a plasma source such as an induction coupled plasma (ICP) is ideal for the dose step.

Fine control of ion energy is required, in the range where most etching thresholds lie: 10 – 50eV. Ideal ALE requires that the adsorbed group have an etch threshold energy distinctly lower than that for etching the substrate – in practice this is hard to achieve, because there may be only a few electron-volts between thresholds, and the ions from a plasma are not monoenergetic.

The gas dose step is critical. Using a standard plasma etcher for ALE will require extended purge times, because the equipment is normally optimized for repeatable, steady state operation. Figure 2 shows the optical emission signal from carbon at 516.5nm in a steady argon plasma, with a steadily increasing dose time of CHF_3 added, from 11msec to 7 seconds. For dose times up to about 200msec, there is a sharp pulse with a rapid decay. For dose times up to about 2 seconds, the decay takes several seconds. Longer dose times do not decay back to floor level, even with 40 seconds before the next gas pulse.

The requirement to switch between chemical dose and non-chemical energetic bombardment puts limits on the cycle time, not because of the ability to create short gas pulses, but because of the time taken to clear the chamber. Optical

emission spectroscopy is a very useful tool, in revealing any buildup of species in the chamber.

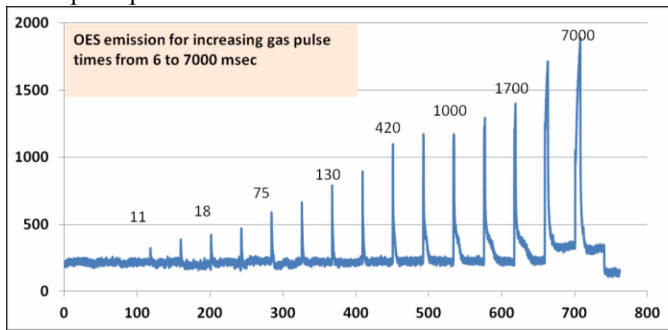

Figure 2. 516nm emission from pulses of CHF_3 added to an argon plasma, with gas pulse times steadily increasing from 6 milliseconds to 7 seconds, spaced 40 seconds apart.

An ALE etch tool is also likely to be required to work as a conventional etcher, if the requirement is to etch down through a large amount of material, and land softly at a critical interface [8].

Etching performance

Benchmarks

As with ALD, ALE etch rates are expressed in etch per cycle (EPC), sometimes without complete transparency on the total cycle length. To qualify as ALE, rather than quasi-ALE (using the cycle, but without any self-limiting characteristics), certain tests must be satisfied.

<u>Synergy.</u> Both the dose and etch steps should be necessary for etching. If significant etching occurs with only one of these present in the cycle, conditions for ALE are not satisfied

<u>Saturation</u> There should be evidence of a plateau in EPC against dose time, etch time, purge time, and etch energy, indicating self-limitation in dose and etching, and adequate purging.

Silicon

ALE of silicon using a chlorine dose and argon ion bombardment in the etch cycle has been studied more extensively. Modeling the cycle [9] now includes non-ideal factors, such as the persistence of background chlorine gas during the etch step and ion bombardment during the dose. Experimentally, widely differing data have been reported on EPC in a plateau regime. [10, 11]. This may be attributable to differing depths of surface amorphisation under ion bombardment, or could be caused by differing amounts of chlorine bonded to surface silicon (SiCl, $SiCl_2$, $SiCl_3$), coupled with different distributions of removed species. (For example, a $SiCl_3$ surface which ejected mainly SiCl would leave surplus silicon to be recycled.

Example data of chlorine/argon ALE of PECVD amorphous silicon from our own work [12] is shown below, using a total cycle time of 7 seconds. PECVD silicon was deposited on SiO2, so that the etch rate could be measured accurately using ellipsometry, after a partial layer etch. The solid line is the EPC with a 40msec chlorine dose, and the dashed line is the EPC with the dose omitted; DC self-bias during the etch step is varied. The graph shows that synergy is satisfied, and there is a partial plateau from 50 volts bias. In this range, argon sputtering is already above threshold, so the plateau is not ideal.

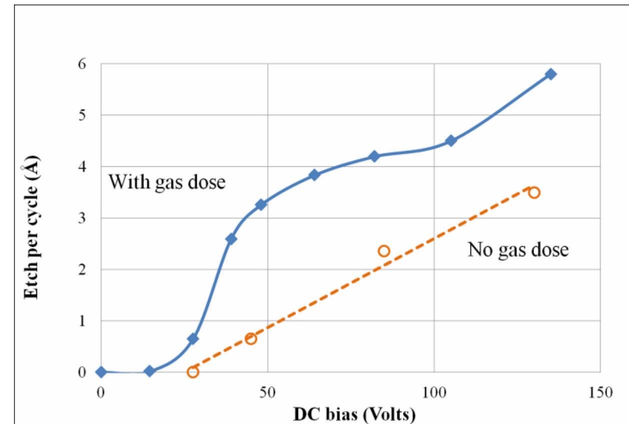

Figure 3. Etch per cycle of amorphous silicon as a function of DC self-bias in the etch phase, with (solid line) and without (dashed line) a 40 msec chlorine gas dose.

ALE could gain ground in mainstream silicon etching, if aspect ratio dependent etching (ARDE) effects are important. The etch depths of high aspect ratio trenches (>10:1) are often significantly less than more open features, limited by loss of etch species to the sidewalls before they can act at the floor, and by transport of reaction products out of the trench. ALD became compelling for its conformality, derived from surface-limited adsorption. ALE offers a similar benefit, where a surface saturation occurs in the dose step, and over-etching is sufficiently selective after adsorbed species are cleared.

Silicon dioxide

The ALE cycle for SiO_2 is not self-limiting. In the dose step, a thin (~2nm) fluorocarbon layer is deposited, which acts as a fixed reservoir of reactants in the etch phase, under noble gas bombardment. This process mimics continuous plasma etching of SiO_2, where the process uses this layer to achieve selectivity to silicon. The cycle places strong demands on the repeatability of the tool, both in chamber condition and in process cycle parameters. Too little polymer will reduce the etch rate for lack of reactants, and too much will also reduce it, by blocking positive ions. If the polymer layer builds up over time, etching will stop.

Figure 4 shows the EPC from an example CHF_3/ Ar ALE cycle, of total duration 40 seconds. This data was taken without a fast chemical dose step hardware kit, so the fluorocarbon polymer deposited was relatively thick at 0.6nm per cycle, seen in the data at zero bias. There is a reasonably broad 20eV window where synergy is perfect, and argon ion

sputtering is almost zero. There is only a hint of a plateau, and this process is classified quasi-ALE.

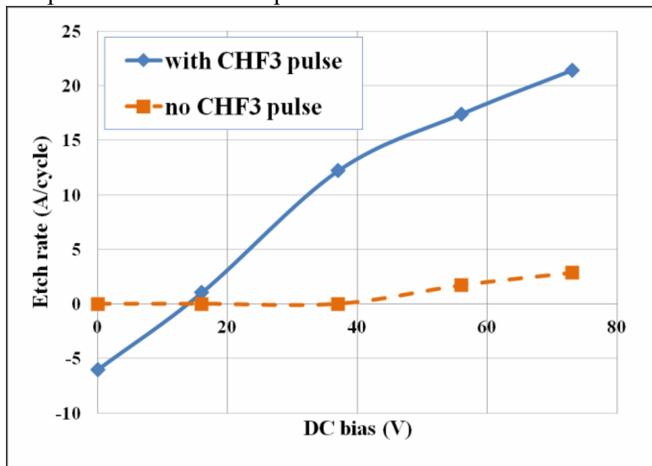

Figure 4 EPC of SiO_2 and argon etching, varying the DC self-bias, with (solid line) and without (dashed line) a CHF_3 gas dose.

This style of process may find application for clearing native oxides at critical interfaces, such as ohmic electrical contacts. However, the use of polymer may prove problematic, because using oxygen plasma to clear it risks re-growing the oxide.

Molybdenum disulphide

There is considerable interest in the broad class of two dimensional (2D) materials, especially transition metal dichalcogenide (TMD) semiconductors such as MoS_2, because electron mobility may be preserved even as the layer thickness is reduced to single digit monolayers. The material was etched in the same chlorine/argon cycle as silicon, and measured by Raman spectroscopy, for different numbers of ALE cycles [13]. The change in separation of the two principal peaks around 400 cm^{-1} indicates that etching is taking place; 40 cycles removed the entire layer. The absence of a peak at 227 cm^{-1} is particularly interesting, because it is attributed to damage in MoS_2. It seems that ALE is able to proceed in this case with very little disruption to the underlying lattice.

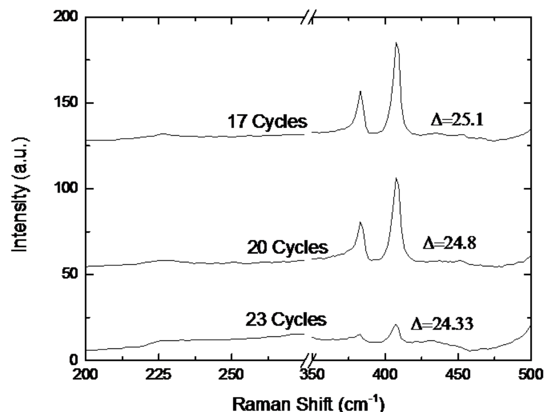

Figure 5. Raman spectra of MoS_2 exposed to argon/chlorine ALE cycles.

When heterostructure devices are finally demonstrated using a stack of 2D materials (e.g. hexagonal boron nitride insulator, graphene conductor and TMD semiconductor) – and not by mechanically assembling flakes – it is likely that a patterning process will be needed which can remove one very thin layer, without disrupting the next atomic layer.

Conclusions

Atomic layer etching is applicable to a range of materials, rather than being limited to a few special cases, thereby earning its name as a distinct technique. It is transitioning from a curiosity to a usable technique, with the appearance of specialized ALE equipment from several vendors. It is beginning to find application areas where its special properties (reduced aspect ratio dependence, and low ion bombardment energy) are useful advantages. If it follows the path of ALD, more applications are sure to follow.

Acknowledgements

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References

[1] S. D. Athavale and D. J. Economou, "Realization of atomic layer etching of silicon" *J. Vac. Sci. Technol., B* 14, 3702, 1996. http://dx.doi.org/10.1116/1.588651

[2] T. Meguro, M. Hamagaki, S. Modaressi, T. Hara, Y. Aoyagi, M. Ishii, and Y. Yamamoto, "Digital etching of GaAs: New approach of dry etching to atomic ordered processing" *Appl. Phys. Lett.* 56, 1552, 1990. http://dx.doi.org/10.1063/1.103171

[3] D. Metzler, R. L. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, "Fluorocarbon assisted atomic layer etching of SiO2 using cyclic Ar/C4F8 plasma" *J. Vac. Sci.Technol. A* 32, 020603, 2014 http://dx.doi.org/10.1116/1.4843575

[4] W. S. Lim, Y. Y. Kim, H. Kim, S. Jang, N. Kwon, B. J. Park, J-H Ahn, I Chung, B. H. Hong, and G. Y. Yeom, "Atomic layer etching of graphene for full graphene device fabrication" *Carbon*, 50, 429, 2012 http://dx.doi.org/10.1016/j.carbon.2011.08.058

[5] F. Wu, G. Levitin, and D. W. Hess, "Mechanistic considerations of low temperature hydrogen-based plasma etching of Cu" *Journal of Vacuum Science and Technology* B 29, 011013, 2011. http://dx.doi.org/10.1116/1.3520461

[6] S. M. George and Younghee Lee, "Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reaction", *ACS Nano* 10, 4889-4894, 2016. http://dx.doi.org/10.1021/acsnano.6b02991

[7] G. C. DeSalvo, C. A. Bozada, J. L. Ebel, D. C. Look, C. Barrette, L. A. Cerny, R. W. Dettmer, J. K. Gillespie, C. K. Havasy, T. J. Jenkins, K. Nakano, C. I. Pettiford, T. K. Quach, J. P. S. James Sewell, and G. D. Via, "Wet Chemical Digital Etching of GaAs at Room Temperature" *J. Electrochem. Soc*., 143, 3652, 1996. http://dx.doi.org/10.1149/1.1837266

[8] A. Goodyear and M. Cooke, European patent "Cyclical Plasma etching" EP16187143, Priority date 3 September 2015.

[9] C. M. HuardYiting Zhang, S. Sriraman, A. Paterson, K. J. Kanarik and M. J. Kushner "Atomic layer etching of 3D structures in silicon: Self-limiting and nonideal reactions" *J. Vac. Sci. Technol. A* 35, 031306, 2017 http://dx.doi.org/10.1116/1.4979661

[10] S.-D. Park, K.-S. Min, B.-Y. Yoon, D.-H. Lee, and G.-Y. Yeom, "Precise Depth Control of Silicon Etching Using Chlorine Atomic Layer Etching" *Jpn. J. Appl. Phys*., Part 1 44, 389, 2005 http://dx.doi.org/10.1143/JJAP.44.389

[11] S. Tan, W. Yang, K. J. Kanarik, T. Lill, V. Vahedi, J. Marks, and R. A. Gottscho, *ECS J. Solid State Sci. Technol*. 4, N5010, 2015. http://dx.doi.org/10.1149/2.0031506jss

[12] A. Goodyear and M. Cooke "Atomic layer etching in close-to-conventional plasma etch tools" *J. Vac. Sci. Technol. A* 35, 01A105, 2017 http://dx.doi.org/10.1116/1.4972393

[13] E. Mercado, A. Goodyear, J. Moffat, M. Cooke, and R. S. Sundaram "A Raman metrology approach to quality control of 2D MoS2 film fabrication" *J. Phys. D* 50, 184005, 2017 http://dx.doi.org/10.1088/1361-6463/aa6786