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AN ANGEL BUSINESS COMMUNICATIONS PUBLICATION

Atomic layer etching: What for?

Atomic layer etching promises to improve the quality of GaN-based HEMTs and eradicate the damage associated with high etching rates

BY MIKE COOKE AND ANDY GOODYEAR
OXFORD INSTRUMENTS PLASMA TECHNOLOGY

ALL THE LATEST MARKET TRENDS from the Internet-of-Things to mobile technology and driverless cars have a common thread: hi tech on the move. This is propelling the industry along a well-trodden path of ever greater functionality, in a smaller and smaller space, while consuming less and less energy. Progress on all these fronts has hinged on the growth of ever thinner films and smaller device features. To do this, there is a need to create and control materials with ever increasing accuracy.

For thin-film deposition, a technology that delivers the goods is atomic layer deposition (ALD). In comparison, conventional plasma etching, which is based on a continuous 'analogue' process, fails to offer the same degree of control. But atomic layer etching (ALE) could change all that and propel plasma etching into its 'digital' age.

	kJ/gmol	eV/bond
Si-Si	531	5.5
Ga-As	210	2.2
In-P	198	2.1
Si-O	799	8.3
Si-N	439	4.6
C-C	607	6.3

Table 1. Bond strengths of diatomic molecules, from the *CRC Handbook of Chemistry and Physics,* 1980

The inherent drawback of plasma etching is that it has to accomplish two contradictory tasks: to etch a material quickly, with good selectivity to a mask material; and to leave the exposed surface undamaged. Success is not easy, given that it is hard to imagine anything more damaging to a material than to break its solid atomic bonds, form new volatile compounds and pump these away as gas.

Yet that is precisely what is undertaken to fulfil the first goal: the surface is exposed to chemical radicals and bombarded with energetic positive ions. These act in synergy to allow volatile compounds to be formed. For example, the etching of InP in a methane/hydrogen plasma involves the formation of volatile trimethyl indium and phosphine.

Often, the ion energy used for plasma etching is ten times higher than the bond strengths of solid compounds (see Table 1). This energy is so high that it can render several atomic layers of the surface amorphous. This promotes rapid etching by allowing chemical radicals to penetrate the surface, but a common major drawback is failure to fulfil the second

goal, which is to form a pristine surface. A more promising approach is that of ALE. This offers a way to etch with far less damage, using the same synergy of chemical radicals and ion bombardment. However, the key difference is that this time there is a cyclical process of chemical exposure and ion bombardment, using ion bombardment energies much closer to the threshold for breaking bonds (see Figure 1). One of the strengths of ALE is that it offers the possibility of self-limiting reactions, which can remove material with the precision of one atomic layer per cycle.

At Oxford Instruments Plasma Technology of Yatton, UK, we have recently released etch tools that are capable of ALE. Associated with this effort, we have demonstrated that the adsorbed gas is really responsible for the etching, by modifying the cycle so that it omits either the gas step or the ion bombardment step: both are essential for etching to proceed. We have found that the gas that is adsorbed forms a reservoir for plasma etching under ion bombardment, and if the bombardment step energy is low enough, etching stops when the reservoir is exhausted.

Another attractive feature of ALE is that, like atomic layer deposition, if a self-limited reaction takes place, this can produce a plateau where the etch rate per cycle is less sensitive to variations in process variables. We have observed this when etching silicon – there are conditions where the etch rate varies only slowly over a range of RF bias power in the ion bombardment step (see Figure 2).

It would be wrong, however, to view ALE as the mirror image of atomic layer deposition. There are constraints in etching, such as selectivity, so the preferred process is likely to be in the initial steeply varying part of the curve. This places increased emphasis on the precision of delivery at around 10 W RF bias power, which needs to be reproducible to within 0.1 W.

An insight into what is taking place in the ALE cycle is provided by optical emission spectroscopy. This technique can track, throughout the cycle, light emission from chlorine and silicon species in the plasma (see Figure 3).

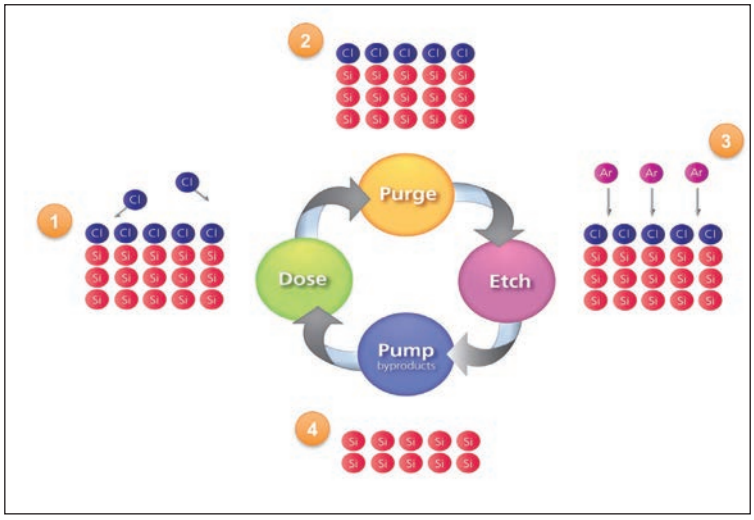

Figure 1. The atomic layer etch cycle. A chemical dose adsorbs on the surface and excess gas is purged away. An etch step under ion bombardment removes the adsorbed radicals together with their chemisorbed partners, ideally stopping once the chemical reactants are exhausted. A pump step may be necessary to clear reaction products before the next chemical dose. Note that this process was proposed more than 20 years ago (see S.D. Athavale *et al*. J. Vac. Sci. Technol. B **14** 3702 (1996)).

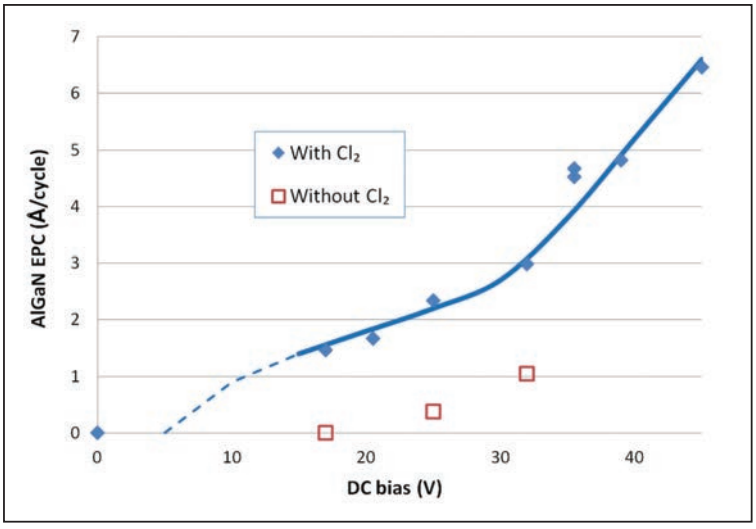

Figure 2. The etch per cycle of amorphous silicon with and without chlorine dosing in an ALE cycle using argon plasma, as a function of the DC bias voltage created by RF power applied to the wafer.

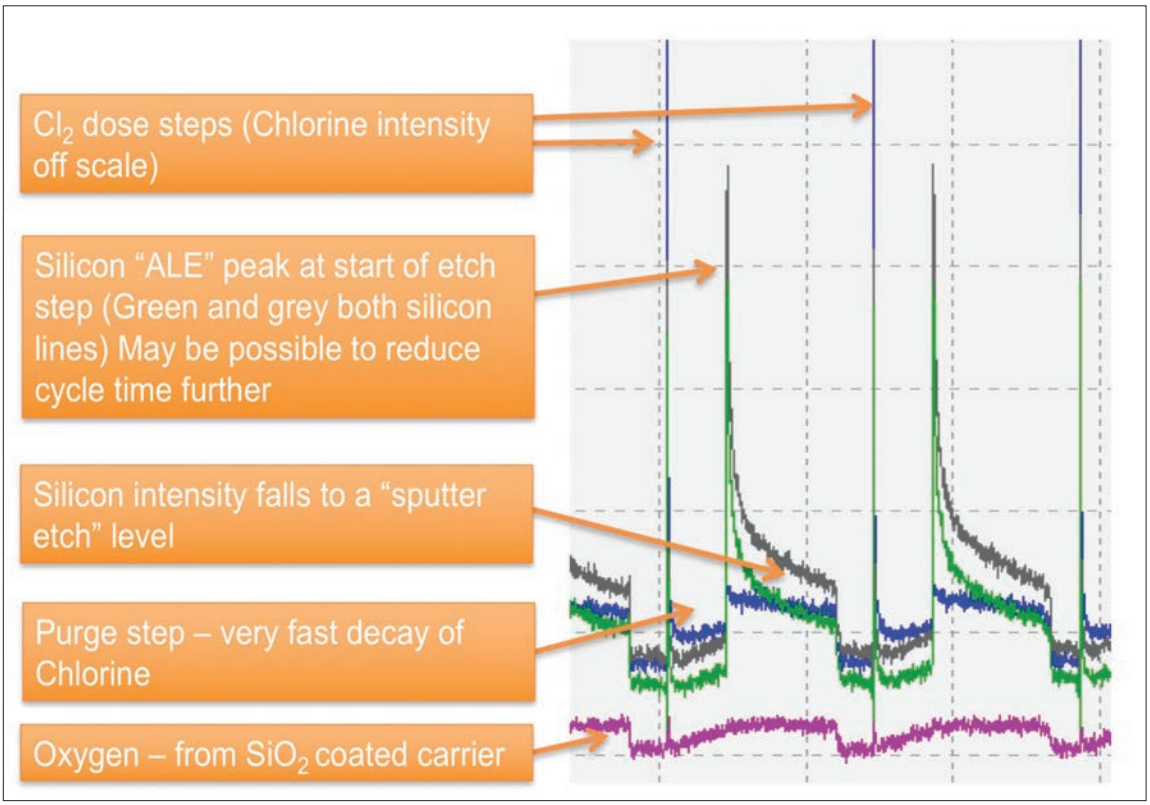

Figure 3. Optical emission spectra of silicon, chlorine and oxygen lines during cycles of atomic layer etching of silicon.

By analysing the results of this spectroscopic measurement, we have found that the chlorine floor level remains constant throughout the cycle, rather than building up over time. This indicates that the pumping-out step between the dose and etch steps is sufficient.

We have also observed a rapid removal of silicon, followed by a decay in light from silicon species. This points to the end of silicon etching, once the adsorbed chlorine has been used. Note that it is essential that new chemical reactants do not reach the surface during the ion bombardment step. If that were the case, the process taking place would not be ALE, but simply standard plasma etching.

Opportunities for ALE

A key question for the future of ALE is whether this process technology is going to be a curiosity, limited to a few examples, or a new general technique. On the plus side, the list of materials etched by ALE is growing, along with interest in the method, as shown by the rising volume of patent applications in recent years.

One of the opportunities for ALE is in the power electronics industry. For the normally off GaN HEMT, a critical step in the production process is the etching of the gate – the GaN cap layer is removed, before a thin AlGaN layer is etched part way through. To ensure a high-performance device, the material that remains must be as undamaged as possible. As the etch depth is only 10-20 nm, a slow, very reproducible etch rate is needed.

ALE is more than up to this task. Success has been proven by HRL Laboratories – it has demonstrated excellent uniformity of threshold voltage across full wafer size. In addition, using our system, we have demonstrated that it produces a surface roughness below 300 pm in AlGaN, even after 200 etch cycles, so it has capability far beyond what is required. We are currently involved in several projects, such as the ALEGRO project, to demonstrate the capability of the ALE technique to enable normally off operation.

The history of Atomic Layer Etching

The acronym ALE was originally used for atomic layer epitaxy, but this evolved into atomic layer deposition (ALD) as the technique developed. Curiously, atomic layer etching emerged in the same conferences – the International Atomic Layer Epitaxy Symposium, in Helsinki 1990 and Raleigh, USA, 1992 – but the technique was described by other names. In 1992 Y. Aoyagi *et al.* published a paper at this conference entitled *Atomic layer manipulation of III-V compounds* (Thin Solid Films **225** 120 (1993)), where they named the layer-by-layer subtraction of material MLE, short for molecular layer etching. Others at the same conference called the technique 'digital etching' (e.g. J. Yamamoto *et al.* Thin Solid Films **225** 124 (1993)). Athavale and Economou started referring to 'atomic layer etching' from 1995 (J.Vac.Sci. Technol **A13** 996 (1995)), using the acronym ALET to distinguish etching from epitaxy. This acronym, sometimes written 'ALEt', has persisted, but is now more commonly abbreviated to ALE.

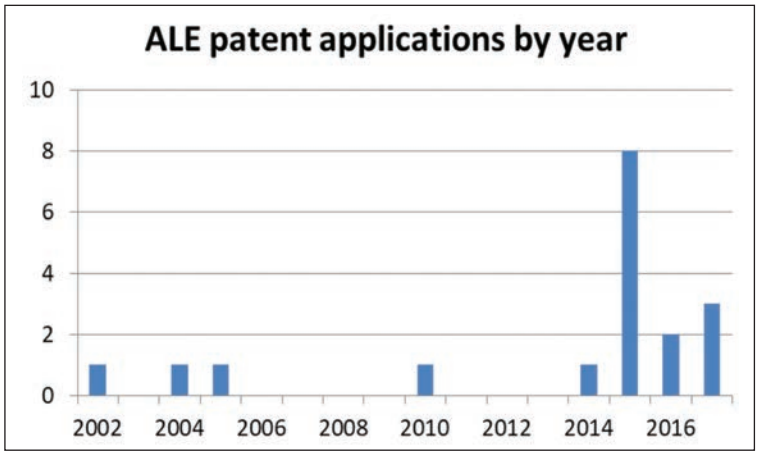

Figure 4. Patent applications citing 'atomic layer etch' by year. Date of first filing of patent family.

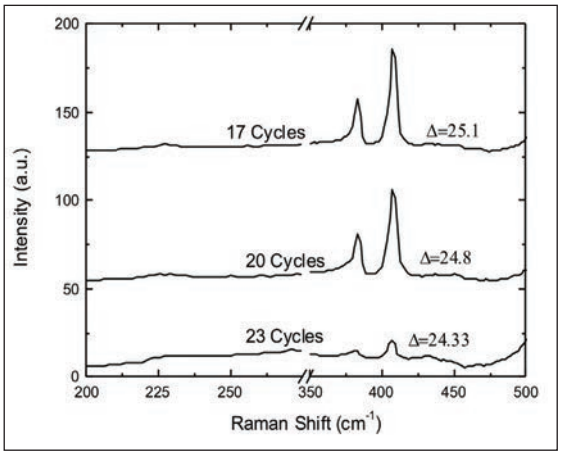

Figure 5. Raman spectra of MoS_2 after a number of ALE cycles. The peak separation narrows, indicating removal of layers, and no damage peak builds up at 227 cm^{-1}.

A related opportunity exists in CMOS manufacturing, because a similar etch is used to remove a gate stack down to a gate dielectric. This opens the gate dielectric at source and drain. A high-quality etch is needed, as any residual damage adds to contact or channel resistance.

Peering in to the future, there could become a time when active devices are formed from one or more layers of atomically thin two-dimensional materials, such as graphene or transition metal dichalcogenides. ALE could have a role to play here. We have used this technique to etch MoS_2 with very low damage. The lack of damage is revealed by Raman spectroscopy, which has the absence of a peak at 227 cm^{-1} that is known to be characteristic of disrupted material (Figure 5). The evolution of a pair of peaks in the Raman spectra also offer evidence that the material, just a few atomic layers thick, was etched during the process.

A hybrid approach

Further opportunities exist as uses for ALE, thanks to its ability to deliver low damage etching. However, as the ALE rate is too slow to process more than a few tens of nanometres economically, it is often best to begin with a traditional high rate etch, before switching to ALE to remove the damaged surface layer. 'Soft landing' etches have been used before, but ALE combines etching at the lowest ion bombardment energies with a very high level of precision.

We have a tool that combines both processes in a single process module. We selected for our starting point the PlasmaPro 100 etch module with 3 kW inductively couple plasma source and a 600 W bias power to the table.

One of the key modifications we made to this tool is to the gas dose hardware. It can now support gas pulses with a duration down to 10 ms, controllable to 1 ms, fed from a low-pressure source. This allows very low doses of gas to be admitted with very fine control on the dose quantity. The mass flow controllers for the pulsed gases reside in an external gas box, as normal.

Additional alterations that we made include a low bias control, allowing both full bias power and fine control in a very low bias range. Note that the hardware is not dependent on a specific model of RF generator. In addition, we have enabled the tool to handle fast cycle recipes, with step times controllable to 1 ms, from a minimum step time of 10 ms.

Thanks to all these modifications, our standard plasma etcher has a far wider processing space. It can now operate in a low bias regime, suitable for standard etching; and it can operate in the atomic layer etch process regime, without the need to invest in a dedicated ALE module.

Material	Gases
Silicon	Ar, Cl_2
GaAs	Ar, Cl_2
GaN	Ar, Cl_2
AlGaN	Ar, Cl_2 or Ar, N_2O, BCl_3
Cu	Cl_2, H_2
Al_2O_3	$Sn(acac)_2$, HF
SiO_2	Ar, CHF_3
Graphene	Ar, O_2

Table 2. Materials etched by ALE.

Further reading
A Goodyear, M Cooke European patent application EP16187143 (3 September 2015)