The Oxygen Contamination Problem for Plasma Enhanced ALD and PECVD

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Is there an oxygen contamination problem for ALD grown nitride materials?

The short answer to this question is, yes. The table over-page shows reports of oxygen content in nitride materials grown by ALD. With its slow growth rates, percentage amounts of contamination are almost universally seen for nitrides grown by ALD.

What are the causes?

There are, of course, a number of well-known contamination sources, insufficient purity of source gases and background contaminants in the vacuum system being the two best known. These can be addressed with gas purifiers, and by improving the vacuum system with the use of load locks, adequate attention to system leaks and having a good quality pumping system. However, even after all these issues have been attended to, researchers have found that a lesser known third source of oxygen contamination can still result in percentage amounts of oxygen in films.

For microwave plasma and inductively coupled plasma (ICP) sources there can be quite severe oxygen contamination from plasma based etching of the dielectric liners used to contain the plasma. The release of parts per million of oxygen into the gas flow can result in percentage amounts of oxygen in a film since many materials '*getter*' oxygen. Though not widely realized, this has been a known problem for well over 20 years. As long ago as 1989 Johnson et. al. [1] reported 1% oxygen contamination in silicon (a material that is not a strong getter of oxygen) from a remote plasma source with a quartz lining. Replacing the quartz with alumina they were able to reduce the contamination.

Figure 1: Quartz lining of an ALD system's ICP plasma source, etched through over time.

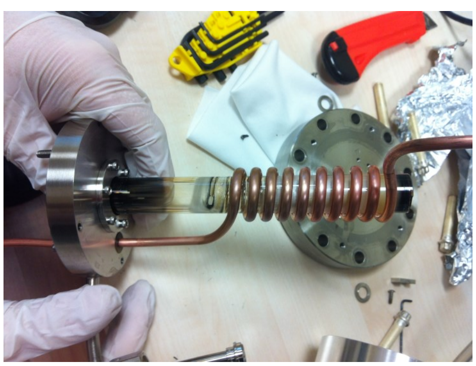

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Table 1 - Is there an oxygen contamination problem for ALD grown nitride materials?

TiN

- 5% and greater oxygen contamination with ICP source, Microelectronic Engineering 86 (2009) 72.
- 18% oxygen contamination with ICP source, ECS Journal of Solid State Science and Technology 3 (2014) P253.
- 20-30% oxygen contamination with ICP source, J. Vac. Sci. Technol. A 31 (2013) 021503.

GdN

- 5% oxygen contamination with ICP source, J. Crystal Growth 338 (2012) 111.

NbN

- 11% oxygen contamination with ICP source, Supercond. Sci. Technol. 26 (2013) 025008.

VN

- 2% oxygen contamination with unspecified remote plasma system, Applied Physics Letters 102 (2013) 111910.

AlN

- 3-35% oxygen contamination with ICP source, Appl. Phys. Lett. 103 (2013) 082110.
- 9% oxygen contamination with ICP source, J. Crystal Growth 421 (2015) 45.

GaN

- 12% oxygen contamination with ICP source, Nanotechnology 26 (2015) 014002.

HFN

- 5% oxygen contamination with home-made ICP plasma source, J. Korean Phys. Soc. 56 (2010) 905.

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A hollow cathode plasma source with nitrogen plasma. The orange colouration is due to the strong activation of molecular species.

Does it matter?

This depends on the material, and the properties desired. For instance, silicon nitride is known to often have oxygen contamination from plasma sources. Goto et. al. reported 7% oxygen contamination from a PECVD plasma source as long ago as 1996 [2]. In fact, oxygen contamination of silicon nitride is a common phenomenon. However, silicon nitride is usually used for its dielectric properties, or as a diffusion barrier, oxygen contamination can cause some variation in dielectric properties, but often this is only a problem if it affects the reproducibility of a process. Consequently, a high level of oxygen may not be problematic in this case, though a variation of oxygen content from run to run might be.

For other materials, percentage amounts of oxygen contamination can defeat electronic properties and are unacceptable. High oxygen content in GaN would make this material useless for many applications.

In the case of TiN - a material commonly used as an electrically conductive diffusion barrier between copper and silicon - the material's resistivity rises with oxygen and carbon contamination (see, for instance table 1 in [3]). A low resistivity is required to reduce processing delays in silicon based electronics, so oxygen contamination should be minimized for best results.

Of course, for research purposes, when looking at fundamental processes for new materials, such as rare earth nitrides, oxygen contamination can be highly detrimental.

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Is it bulk oxygen contamination or is it from atmospheric exposure?

Oxygen contamination can also result from ex-situ exposure to air for polycrystalline materials [4-6]. Grain boundaries can act as pathways for the diffusion of adventitious hydrocarbons, water vapour and carbon oxides. Quite often these atmospheric contaminants can be distinguished using XPS as hydroxides, and the well-known adventitious hydrocarbon peak used for calibration, are easily identified in comparison to bulk grown contaminants [7]. Though, for such analysis, reduction of the surface species by argon ion etching or by the X-ray beam can occur and should be monitored [7].

Complicating this problem, for some materials, the solubility of oxygen in the nitride can be quite low, so excess contamination during film growth will segregate in a separate phase, quite possibly at grain boundaries. This type of contamination has been observed for GaN [6]. This means that increased oxygen contamination will result in smaller grains of GaN and may ultimately result in the formation of an amorphous material [6,8].

The monitoring of grain size by X-ray diffraction, or AFM, TEM or SEM imaging, can therefore be important diagnostics for determining the origin of such contamination.

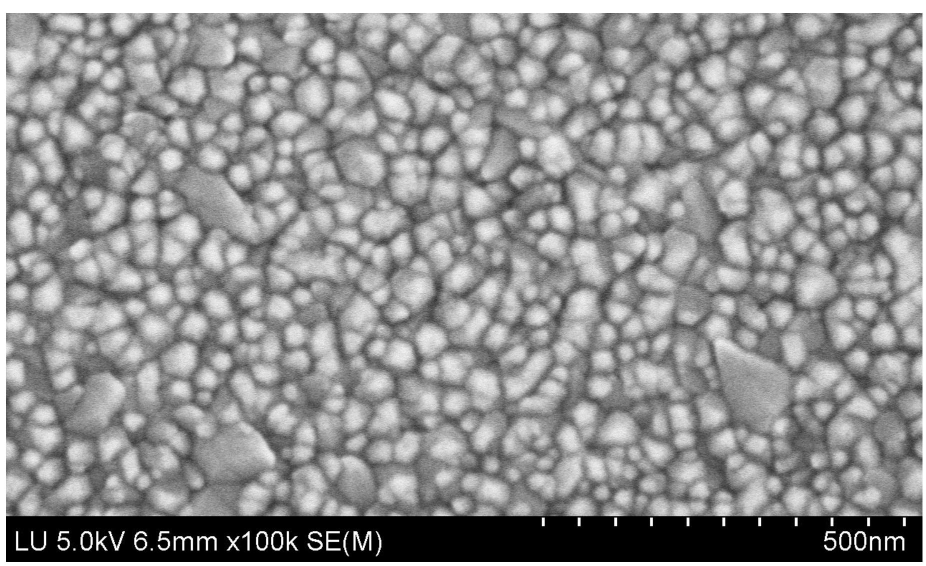

Figure 2: High resolution SEM image of polycrystalline GaN with crystal grains evident at the surface. Diffusion of adventitious atmospheric species would be expected down the grain boundaries – adding to oxygen and carbon contamination.

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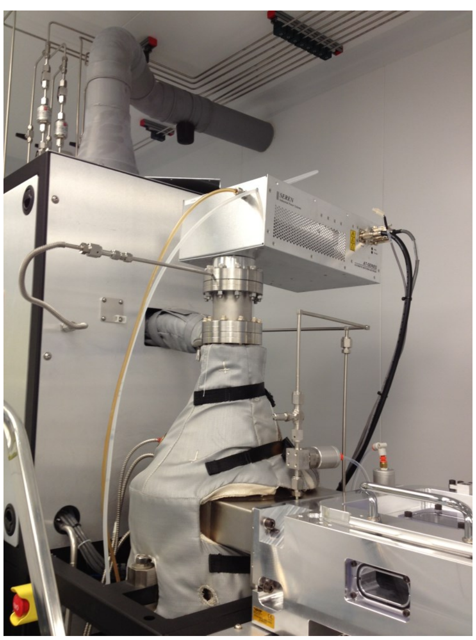
X-ray Photoelectron Spectroscopy (XPS) measurement limitations

With the coarse contamination levels often present, many ALD researchers rely on XPS as a standard diagnostic. However, this is a background limited chemical analysis technique. That is, the oxygen background in the UHV chamber of an XPS system will set the minimum amount of oxygen contamination that can be legitimately measured. Surface oxides are, of course, always present. Bulk measurements are usually performed after argon ion etching of the surface, however knock on of surface oxides can occur [7,9-11] as well as preferential loss of the nitride species [7,9,12].

The minimum level of oxygen that can be measured will vary from system to system and material to material. Using a hollow cathode plasma source, Bilkent University were able to measure down to limits of 2.5-3.0% for AlN and 1.5-1.7% for GaN [10]. Whereas other systems have shown higher limits for the same materials, eg.[9].

To measure the actual oxygen levels in their films, Bilkent University had to rely on SIMS (secondary ion mass spectroscopy) rather than XPS. Luckily, SIMS technology has developed to the point where it can be used for the very thin layers grown using ALD. They determined that the oxygen in their films was lower than observed by XPS, at 0.7% for AlN and 0.1-0.2% for GaN with this residual likely to be from atmospheric exposure of grain boundaries. To date, these are some of the lowest oxygen contamination levels that have been achieved for AlN and GaN grown by ALD. Because of the lower oxygen contamination provided by their hollow cathode plasma source [10], Bilkent University have since been able to successfully produce electronic devices based on this material at very low growth temperatures [13-15].

Bilkent University's ALD system, converted to hollow cathode plasma source operation.



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Solutions to the ICP/microwave plasma oxygen contamination problem

Substituting alumina tubes for quartz can lead to some improvement [1]. However, it has been shown that oxygen contamination can still be problematic with alumina or sapphire based tubing [16]. This is important to note, since some current manufacturers of PE-ALD equipment use alumina tubes for their ICP sources.

The company BluGlass Ltd, have utilized a long period (up to 72 hours) of plasma conditioning to prevent oxygen contamination from the quartz that was used in their microwave plasma sources prior to remote plasma CVD [17]. However, exposure of the tube to air, or to hydrogen based gases, such as ammonia, could strip this passivation away. In that case the long passivation cycle had to be repeated.

Our company Meaglow Ltd, has gone a different direction, looking toward a cost effective, easily implemented, '*next generation'* approach to the problem of oxygen contamination from ICP sources. That solution has been to design and manufacture high plasma density, all metal, plasma sources, based on the hollow cathode effect [18,19]. At growth temperatures of ~ 650^{o} C oxygen contamination in GaN has been reduced to levels similar to those seen for MOCVD grown films i.e. ~ 10^{16} cm^{-3} [19].

These patented plasma sources can be retrofit to existing equipment and can be conditioned for use in a matter of hours, rather than days. They can also be effectively used with hydrogen bearing species, including ammonia. The success of the Bilkent group, mentioned above, is the result of their using a Meaglow hollow cathode plasma source as a direct replacement of an ICP source.

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Some of the properties of these sources are indicated in the table below. For the new materials deposited by the ALD community, the hollow cathode plasma source is the '*next generation*' solution to an old contamination problem that '*once upon a time*' didn't matter so much.

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Table 2 - Comparison of general properties of Capacitively Coupled Plasma (CCP), Inductively Coupled Plasma (ICP), Microwave Plasma (MP) and Hollow Cathode Plasma Sources (HC).

Plasma Type	CCP	ICP	MP	HC
Plasma Density	Low	High ✓	High ✓	High ✓
Oxygen Contamination	Low ✓	High	High	Low ✓
Crystallinity	Average	Average	Average	Exceptional ✓
Plasma Damage	High	High	Low ✓	Low ✓
Growth Rates	Low	Medium	Medium	High ✓
Scalability	High ✓	Medium	Low	High ✓

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