

# The impact of consumer demand for cutting-edge display technology on the gases market

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*How gases are used in the manufacture of displays is being impacted by new technologies, consumer demand, and the burgeoning China market.*

**W**hile the display market is no longer enjoying double-digit annual growth rates, it is experiencing resurgence due to increasing customer demands for larger flat-panel displays, OLED and 4K technology, ultra-slim form factor, curved and wearable displays, automotive displays, and more. This growth is particularly conspicuous in China, a late comer to the market, which is now the fastest growing region in display manufacturing.

These new technologies and markets require very large quantities of ultra-high purity bulk and electronic specialty gases and a dependable supply chain for these gases. This article will explore the impact of these technologies, consumer demand, and the burgeoning China market on the gases used in the manufacture of display.

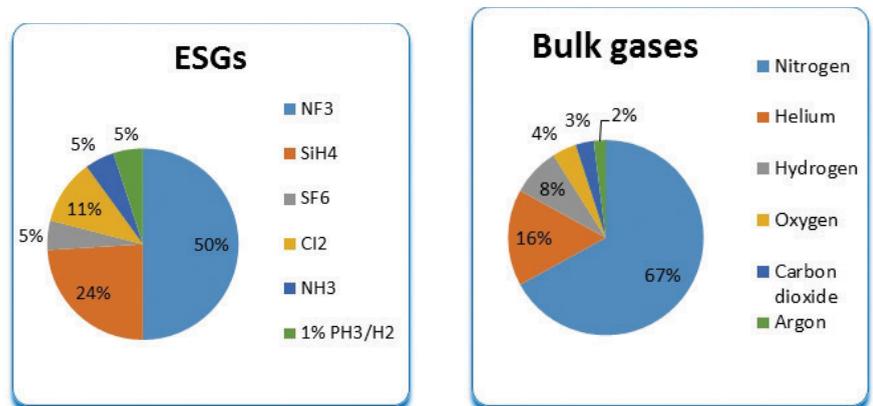
## Display market

According to IHS DisplaySearch, in 2014 the global display market saw revenue of \$134 billion and is expected to grow 6% in 2015. The demand is being driven in large part due to new technologies and new uses for existing display technologies such as 4K, OLED, curved, and flexible displays.

## Gases used in display

This love affair that consumers have of interacting with devices large and small not only increases the volume of displays to be manufactured, it also increases the volume of gases needed to make the displays. In the 20 years since the initial development and commercialization of the first Thin Film Transistor (TFT) LCD display panel, the gases market for the display sector has grown to around \$450 million.

As shown in **FIGURE 1**, display manufacturing today uses a wide variety of gases, which can be categorized into two types: Electronic specialty gases (ESGs) and Electronic bulk gases (EBGs).



**FIGURE 1.** Market breakdown for the two types of gases used in display manufacturing.

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TABLE 1.

Gases used in manufacture of display				
	◇ = nominal amount ▼ = less than nominal X = not typically used	a-Si	LTPS	MO
Thin Film	SiH <sub>4</sub> (Silane)	◇	◇	▼
	NH <sub>3</sub> (Ammonia)	◇	▼	▼
	N <sub>2</sub> O (Nitrous oxide)	x	◇	◇
	TEOS (Tetraethyl orthosilicate)	◇	◇	▼
Doping	1% B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> (Diborane/Hydrogen)	x	◇	x
	15% B <sub>2</sub> H <sub>6</sub> /H <sub>2</sub> (Diborane/Hydrogen)	x	◇	x
	1% PH <sub>3</sub> /H <sub>2</sub> (Phosphine/Hydrogen)	◇	◇	x
	20% PH <sub>3</sub> /H <sub>2</sub> (Phosphine/Hydrogen)	◇	◇	x
	1% PH <sub>3</sub> /SiH <sub>4</sub> (Phosphine/Silane)	◇	◇	x
Clean	NF <sub>3</sub> (Nitrogen trifluoride)	◇	◇	◇
	F <sub>2</sub> (Fluorine)	◇	◇	◇
Etch	CF <sub>4</sub> (Carbon tetrafluoride)	◇	◇	◇
	C <sub>2</sub> HF <sub>5</sub> (Ethyl chloride)	x	◇	x
	SF <sub>6</sub> (Sulfur hexafluoride)	◇	◇	◇
	Cl <sub>2</sub> (Chlorine)	◇	▼	▼
	C <sub>4</sub> F <sub>8</sub> (Octafluorocyclobutane)	x	◇	x
	BCl <sub>3</sub> (Boron trichloride)	◇	▼	▼
Laser	4.5% HCl/1% H <sub>2</sub> /Ne (Hydrogen chloride/Hydrogen/Neon)	x	◇	x
	Xe (Xenon)	x	◇	x
	Ne (Neon)	x	◇	x
	5% F <sub>2</sub> /He (Fluorine/Helium)	x	◇	x
	Kr (Krypton)	x	◇	x
Bulk	H <sub>2</sub> (Hydrogen)	◇	◇	◇
	O <sub>2</sub> (Oxygen)	◇	◇	◇
	N <sub>2</sub> (Nitrogen)	◇	◇	◇
	He (Helium)	◇	◇	◇
	Ar (Argon)	◇	◇	◇
	CO <sub>2</sub> (Carbon dioxide)	◇	◇	◇

**Electronic specialty gases (ESGs)**

Silane, nitrogen trifluoride, fluorine (on-site generation), sulfur hexafluoride, ammonia, and phosphine mixtures make up 52% of the gases used in the manufacture of displays and are available in both cylinder and bulk supply.

Of the major countries that manufacture displays, Taiwan and China import most of their ESGs while Korea and Japan have robust domestic production of ESGs.

**Silane:** SiH<sub>4</sub> is one of the most critical molecules in flat panel manufacturing. Silane is used for deposition of amorphous Si (silicon), the most critical layer in the TFT transistor.

**Nitrogen trifluoride:** NF<sub>3</sub> is the single largest Electronic Material from spend and volume standpoint for flat panel display (FPD) production. NF<sub>3</sub> is used for cleaning the PECVD (plasma-enhanced chemical vapor deposition). This gas requires scalability to get the cost advantage necessary for the highly competitive market. Over 70% of the global capacity of NF<sub>3</sub> comes from Korea and Japan.

**Electronic bulk gases (EBGs)**

Nitrogen, hydrogen, helium, oxygen, carbon dioxide, and argon make up 48% of the gases used in the manufacture of displays.

**Nitrogen:** For a typical large TFT-LCD fab, nitrogen demand can be as high as 30,000 Nm<sup>3</sup>/hour so an on-site generator, such as the Linde SPECTRA®-N 30,000, is a cost-effective solution that has the added benefit of an 8% reduction in CO<sub>2</sub> footprint over conventional nitrogen plants.

**Helium** is used for cooling the glass during and after processing. Manufacturers are looking at ways to decrease the usage of helium because of cost and availability issues due it being a non-renewable gas.

**New technologies and implications for gases**

Currently about 20% of smartphones – the ones with lower resolution displays – use a-Si display process. Higher resolution devices and new effects such as curved displays require higher performance transistors and improvements in electron mobility. This can be achieved by switching from amorphous silicon (a-Si) transistors to low temperature

TABLE 2.

Transistor type	Electron mobility (m <sup>2</sup> /Vs)	Cost	Manufacturing challenges
a-Si	<1	low	low
MO	1-50 (typically 5-10)	low	high
LTPS	50-300	high	medium

polysilicon (LTPS) or metal oxide (MO), also known as transparent amorphous oxide semiconductor (TAOS).

LTPS is used in about 44% of high-end LCD smartphone displays as it has the highest performance. Due to its higher costs and scalability limitations, LTPS is less suited for large screen displays.

Small displays with very high pixel resolution are produced with LTPS. High-definition large displays can be made using MO. Metal oxide semiconductors can remain in an active state longer than traditional LCD and can cut power consumption by up to 90%, which is a huge benefit.

### New process requirements

#### Metal Oxide TFT and LTPS:

To meet the changes in technology, N<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>F, C<sub>4</sub>F<sub>8</sub>, BF<sub>3</sub>, and laser gases are replacing or at least reducing the requirement of NH<sub>3</sub>, BCl<sub>3</sub>, and SiH<sub>4</sub>.

The use of N<sub>2</sub>O is expected to double from 5,000 TPA (tons per annum) in 2013 to 10,000 TPA in 2017. Why nitrous oxide? The move from a-Si to MO requires a change in the TFT device structure where the a-Si layers (g-SiN<sub>x</sub>, a-Si, n+) are being replaced by the MO layers (g-SiO<sub>x</sub> + indium gallium zinc oxide). This requires a change from NH<sub>3</sub> to high-volume, high-purity N<sub>2</sub>O.

LTPS process also uses N<sub>2</sub>O for its oxide layer deposition. In addition, LTPS uses XeCl (xenon monochloride) excimer lasers for annealing after the

silicon deposition to change the silicon structure to polysilicon. High-performance laser gases, such as Ne, Xe, and Kr from Linde, are well-suited for this process.

**Transparent Conductive Films (TCF) and ITO Replacements:** TCFs are used in most high-tech displays and touchscreens, and particularly in displays that are bent or curved. Currently the electronics industry relies primarily on Indium Tin Oxide (ITO) to make electro-conductive films for display. ITO presents challenges: it is brittle and cracks so new TCFs are needed for structural flexibility.

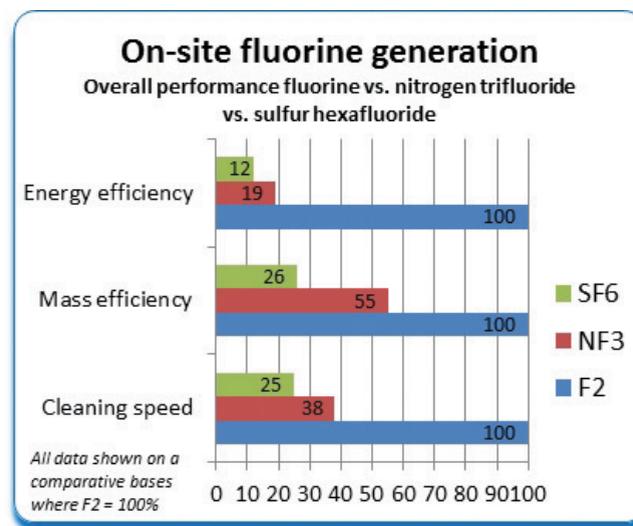
New materials to potentially replace ITO are metal mesh, Ag nanowire (agNW), and carbon nanotube (CNT), which are all highly flexible with comparable transparency and resistance to ITO. Metal mesh is good for large displays, but is restricted on small and medium displays due to its wire width (typically 6

μm). AgNW demonstrates excellent transmittance and flexibility with small wire diameter (20 – 100 nm), but haze is an issue. CNT has excellent conductivity, transmittance, and flexibility, but the supply chain needs to be developed. Single walled carbon nanotubes (SWNT) technology from Linde uses liquid ammonia to produce solubilized carbon nanotubes in the form of inks, which can then be deposited as films and has

the added benefit of zero carbon footprint.

**F<sub>2</sub> as replacement for NF<sub>3</sub> and SF<sub>6</sub>:** For a typical large TFT-LCD fab, chamber cleaning gas demand can exceed 300 tons per year. Traditionally NF<sub>3</sub> has been used. The GWP<sub>100</sub> (100-year Global Warming Potential) for NF<sub>3</sub> is 17,200; for the replacement F<sub>2</sub>, the GWP<sub>100</sub> is 0.

Switching to fluorine not only significantly reduces environmental footprint, but also leads to material



**FIGURE 2.** Switching to fluorine reduces environmental footprint, material costs cleaning time.

cost savings and up to 50% reduction in cleaning time, increasing productivity (**FIGURE 2**).

Fluorine can also be used to replace Sulfur hexafluoride ( $\text{SF}_6$ ), which is used in dielectric etching. The  $\text{GWP}_{100}$  for  $\text{SF}_6$  is 22,800, which surpasses that of  $\text{NF}_3$ . Significant improvements in etch rate and etch uniformity have been measured with the shift to  $\text{F}_2$ .

On-site fluorine generation, like that available from Linde, eliminates large-volume, high-pressure storage, and modular generators meet all flow and volume requirements for the largest scale fabs.

### The China factor

Currently Korea is the leader in display manufacturing, with Taiwan and China on its heels and Japan a distant fourth (**FIGURE 3**). This is changing, though, as China rapidly gains market share. China, which started in most traditional manufacturing industries as “factory to the world,” is a relative late comer in the display sector due to technology barriers.

Currently there are about five major domestic display manufacturers in China; they cater primarily to domestic mobile display and large screen markets. China has been aggressively investing in display fabs over the last five years and has gained market share from other regions.

It is expected that China will account for more than 50% of display capacity investment in the next four years. China capacity is expected to double with aggressive investments especially in the leading technology Low Temperature Polysilicon (LTPS) and Metal Oxide (MO).

### Gas supply issues in China

Bulk gases are produced in China, mostly by large international gas companies. There are domestic producers of some ESGs ( $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{SF}_6$ ); other gases currently are mostly imported.

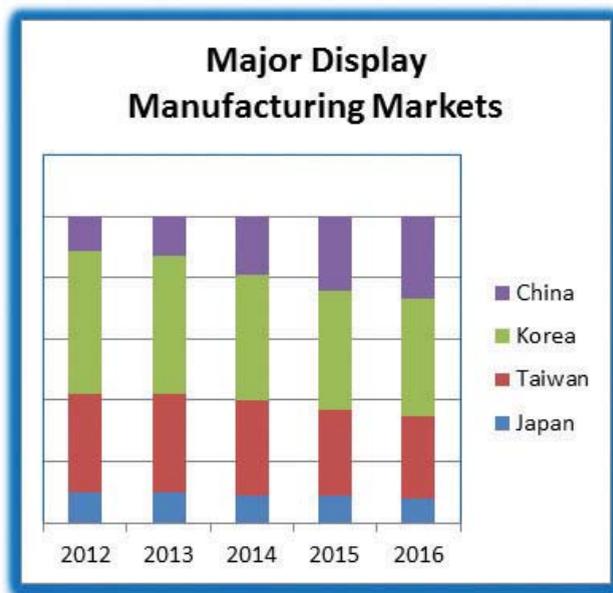
**Silane ( $\text{SiH}_4$ ):** Silane, primarily extracted as an interim process gas during poly silicon production, is one of the most critical molecules in FPD manufacturing.

Chinese producers have a very small capacity of silane as they entered the market late. Considering the need for extensive qualification, technical support to achieve that, and the lack of scalable production base, local Chinese poly silicon producers are not able to offer a complete package and thus China still imports more than 80% of its silane and produces locally only 2% of the global capacity of silane.

The current consumption of silane in China display manufacturing is about 300 TPA, which is 7.5% of the global demand, and is expected to double in the next four years. Considering the complexity

of the supply chain, import regulations, and storage requirements, companies are actively moving towards local transfilling and analytical capability.

**Nitrogen trifluoride ( $\text{NF}_3$ ):** Similar to silane, the China display manufacturing consumption of  $\text{NF}_3$  is expected to double to greater than 2000 TPA in the next four years. Considering the volume used and spend on  $\text{NF}_3$  and the rapid expansion of FPD manufacturing in China, more production will be done locally to minimize customs duties and to support domestic sourcing requirements.  $\text{NF}_3$  is relatively easy to qualify for chamber cleaning, but ISO supply to



**FIGURE 3.** Currently Korea is the leader in display manufacturing, with Taiwan and China on its heels and Japan a distant fourth. This is changing, though, as China rapidly gains market share. Source: IHS Displaysearch and Linde Internal.

large customers is the biggest challenge since most producers do not have large-scale production and equipped facilities to make  $\text{NF}_3$  cost-effective to make. This is a major area of investment for local producers.

#### ***LTPS, Metal Oxide, and the Increase in Demand for***

***$\text{N}_2\text{O}$*** :  $\text{N}_2\text{O}$  is a regional and localized product due to its low cost, making long supply chains with high logistic costs unfeasible. Currently, in the region, Korea manufactures about 63% of high-purity  $\text{N}_2\text{O}$ , Taiwan about 30%, and China only about 7%. As China leap frogs its display industry into the cutting-edge metal oxide, or LTPS nodes, the demand for  $\text{N}_2\text{O}$  will triple from its current requirement to 3,000 TPA in 2017 with the adoption of LTPS and MO.

#### **Enablers of the growth of the China display industry**

The key priorities for materials manufacturers to enable the growth of the China display industry are:

- Commitment to invest in local infrastructures such as on-site bulk gas plants
- Localization of production facilities for high-purity gas and chemical manufacturing
- Collaboration with global materials suppliers for development of new materials

#### **Conclusion**

To accommodate the boundless appetite that consumers have for the latest, most innovative, and highest definition displays – both large and small – display manufacturers must partner with gas suppliers to:

- Identify the most appropriate gas and display technology match-up
- Globally source electronic materials to provide customers with stable and cost-effective gas solutions
- Develop local sources of electronic materials
- Improve productivity
- Reduce carbon footprint and increase energy efficiency through on-site gas plants ◀▶