High purity alumina has flown under the radar, but it has been the critical raw material fuelling significant growth in the LED market, identified last month as one of Goldman Sachs’ low carbon economy industries to watch. The surge in LED demand has seen the technology take a majority market share from the traditional light bulb in little over a decade. But it is not the only role the specialist chemical plays in disruptive technology.

Dr Richard Flook examines key hi-tech markets for high purity alumina and producers positioning themselves for this evolution in demand.
**FEATURE**

Natural sapphire is coarsely (po-aluminous) with traces of metallic elements that can impart a variety of colours including that found in the familiar blue sapphire (iron & titanium) and ruby (chromium). The world retail sapphire gem market has been estimated to be about 40,000 tonnes and worth about $3 bn. However, this market is now being overtaken by production of synthetic sapphire.

Production of synthetic sapphire has been possible for over a century (Vesuvius, 1902 and Czochralski, 1916) but even as recently as a decade ago, annual world production was only a few hundred tonnes. The last decade has shown rapid growth in both production and new applications for synthetic sapphire based on a number of fundamental properties of corundum including its high electrical insulating and thermal conductivity properties and its well-known hardness of 9.0 on the Mohs scale.

The starting material for the production of synthetic sapphire is high purity alumina (HPA) which is usually accepted to be greater than or equal to 99.99% purity (4N or 1000ppm impurities). In 2013, production of HPA was estimated to be about 19,000 tonnes of which about 70% was produced in Asia. Global production is forecast to increase at a CAGR of 28% and reach 48,000 tonnes by 2028.

**HPA production**

There are three main processes for the production of HPA. These processes are the thermal decomposition method, the water soluble/choline process and the alkoxide hydrolysis process.

The thermal decomposition method utilises aluminium aluminium sulphate (NH₄Al(SO₄)₂) or ammonium aluminium carbonate hydroxide (NH₄ACO₃(OH)₂) as starting materials. HPA purity is usually no more than 99.99% since elements such as iron, nickel, titanium, zircon and halogen cannot be easily removed and the product is usually only suitable for optical sapphires. The water soluble or choline method is based on dissolving aluminium in alkali solution and is used by some of the largest producers in China. Depending on the methods and materials, purity can be limited and application is sometimes restricted to optical sapphires.

The alkoxide process, developed by Japanese corporation, Sumitomo, is a recognised process for producing ultra-high purity alumina (5N). In this process high purity aluminium alkoxide is synthesised from aluminium metal and alcohol and hydrated alumina is produced by hydrolysis of the alkoxide. Finally, high purity alumina is obtained by calcination. Impurities can be removed in the distillation stage or with ceramic membranes.

The three major applications of HPA have been estimated to be in the production of light emitting diodes (LEDs) which currently accounts for 60% of HPA production, semiconductors (20%) and phosphors (15%). The major HPA growth market is LED, 90% of which currently use a sapphire substrate and whose production is forecast to grow at a CAGR of 19% to 2024. HPA prices have been estimated to range from $15/kg to $25/kg for 4N HPA, $30/kg to $30/kg for 4N and greater than US$50/kg for 5N.

Although electroluminescence in a crystal of silicon carbide was first discovered in 1967 it was nearly a century later before a commercial LED was developed. The first key event that led to the current LED was the discovery of visible light emission from gallium arsenide phosphide at Bell Laboratories in 1962. The second key event was the discovery in 1966 by Isamu Akasaka and Hiroshi Amano of Nagoya University in Japan of a way of creating gallium nitride (GaN) crystals on a sapphire substrate. The final key event was the discovery of the blue LED using an yttrium aluminium garnet (YAG) phosphor with a blue LED die by Shuji Nakamura at Nichia in Japan. Akasaki, Amano, and Nakamura were awarded the 2014 Nobel Prize in physics for their discoveries.

The first commercial LED was produced by Nichia in 1996 but it took another seven years to develop a technically competitive although still expensive product. Since then luminosity and efficacy of LEDs has doubled approximately every three years following a trend known as Hatfield’s law (analogous to Moore’s law for CMOS-based chips). Meanwhile, prices have plummeted by 20 percent per year in terms of dollars per lumen. Ongoing research is crucial to the advance of LED technology, which is fast becoming an avenue to reduce electricity consumption. According to the United States Department of Energy (DOE), residential LED lighting uses at least 75% less energy than regular incandescent lighting. Since 2003, the DOE has funded over 200 R&D projects and has the goal: “By 2025, develop advanced SSL technologies that — compared to conventional lighting technologies — are much more energy efficient, longer lasting, and cost competitive, by targeting a product system efficiency of 50 percent with lighting that accurately reproduces sunlight spectrum.”

**HIGH PURITY ALUMINA - THE NEW PRODUCERS**

The traditional HPA production processes use relatively expensive raw materials. Two companies are proposing alternative processes based on cheaper raw materials - kaolin and aluminium clay.

Altech Chemicals Ltd

Formerly Australian Minerals and Mining Group Ltd, Altech is proposing to react a relatively low impurity (1.4% Fe₂O₃ + TiO₂) kaolin with hydrochloric acid to produce 4N HPA in a 4,000 tonnes pa capacity plant. Capital cost is estimated at $77M and 55M of project debt is targeted. Selling price 4N HPA is estimated to be $23/kg and operating expenses are estimated to be about $8/kg.


Formerly Exploration Orbité V.S.P.A Inc is currently working on the completion of its three tonnes per day 5N high purity alumina (HPA) production plant which also utilises hydrochloric acid extraction from alumina clay. HPA production is forecast for Q4 2015 and expansion to 5 tonnes per day is planned in 2016. HPA samples of 4N8 (99.998%) purity have been sent to customers.

HPA Sonics LLC.

Little public information is currently available apart from a projected start up in 2015 for 4N and 5N HPA.

**LED SUPPLY CHAIN: FROM MINE TO MARKET**

High purity alumina

Sapphire ingot

Sapphire wafer

Epi growth

LED chip

LED package

**HIGH PURITY ALUMINA**

**IN NUMBERS**

>85%

The energy saving from LED over a traditional light bulb

19%

The average CAGR expected in LEDs over the next decade

19,000

Global high purity alumina output in tonnes in 2015

60%

LEDs are the dominate consuming market for HPA consuming over half of its output

Source: Goldman Sachs, Altech, Technics Research

**LED and Sapphire - cost reduction & larger wafer size**

Production of sapphire starts with a seed sapphire crystal, a mixture of high purity alumina and un-crystallized sapphire material (crackle) which are heated in a crucible. Manufacturers crystal growth techniques are generally grouped under five methods: Kyropoulos method (KY), heat exchanger method (HEM), Czochralski method (CZ), edge-defined film-fed growth method (EFG) and the temperature gradient technique (TGT). After slow cooling, the single crystal ingot or boule is examined for defects such as gas bubbles, cracks and contamination which can cause defects in the epitaxy process (oriented gallium nitride crystal growth). The section of the boules not used is recycled into the original growth process. The boule is then “core-drilled” to produce...
LED Sapphire Competitors - silicon carbide and silicon substrates

The majority of LED manufacturers use a sapphire substrate in all or most of their products. Notable exceptions include Cree Inc. (silicon carbide), Soraa Inc. (gallium nitride) and Flexxsi Semiconductors (silicon).

The main factors determining the appropriate substrate materials are matched lattice parameters and thermal expansion coefficients as well as good crystallinity, chemical, physical and mechanical properties.

Gallium nitride and silicon carbide substrates have higher cost than sapphire although both have a better lattice match with the gallium nitride crystal.

Silicon has a poorer lattice match with gallium nitride but is attractive on cost compared to sapphire substrates. By using silicon substrates, manufacturers can capitalise on the existing manufacturing infrastructure that the semiconductor industry uses.

This, coupled with the lower price of raw materials and processing costs, makes silicon a very tempting replacement for sapphire wafers. Three problems are the accommodation of the larger lattice mismatch with growth of the epilayer layer of gallium nitride, the large difference in the coefficient of thermal expansion of silicon and gallium nitride and silicon’s absorption of photons.

However, Toshiba appears to have overcome some of these problems and first launched a range of gallium nitride on silicon products in late 2012. By 2020, some forecasters predict that approximately 10% of all LEDs will be using silicon substrates and about 18% will be using silicon carbide. Based on these forecasts, the LED sapphire substrate market share could drop from about 90% to about 70-75% although of a much larger market.

Smartphones and batteries

Apple was the pioneer in introducing sapphire glass into Apple’s iPhone 5 Camera lens, and iPhone 5S home buttons. However, the HPA and sapphire market was shattered by Apple’s decision not to proceed with a sapphire cover glass in the iPhone 6.

Since then it has been reported that some Chinese smartphone manufacturers (including Huawei), Vivo and Dake have followed Apple’s adoption of sapphire substrates in smartphones but most manufacturers are only employing sapphire glass screens in high end smartphones.

Although sapphire crystal glass is stronger than Corning Gorilla glass, transparency can be lower and can lead to some optical distortion. Also, sapphire glass is 67% heavier than a same sized glass and up to ten times more expensive.

If all smartphones were converted to sapphire glass the market for HPA would increase by about 15,000 tonnes pa. It is now thought that phones with sapphire screens are more likely to be seen in niche applications. However, this market for HPA has such a large potential it is worth watching.

HPA is also used to coat the ceramic separators in the high growth lithium ion batteries (LIB) market whose demand in turn is driven by growth in the Electric Vehicle (EV) and Plug in Hybrid Electric Vehicles (PHEV).

The insulating properties of the ceramic separator are controlled by the packing of different sizes of HPA. Sumitomo Chemicals started manufacturing HPA (AKP 56 & AKP-3000) from a 1,600 tonnes pa capacity plant for LIB applications in South Korea in 2013. Sumitomo have recently been granted a patent for HPA coated plastic separators that stop excessive and abnormal heat generation by melting and shutting down ion passage in LIB (US2015/0155541 A1 June 2015). Evonik offer a competitive fumed alumina (Aeroxide Alu) for LIB separators.

The market for HPA in silicon on sapphire (SOS) semiconductors which are used in radio frequency integrated circuits (RFIC) is considered to have a steady and moderate growth rate. Other sapphire applications including military applications are relatively stable.

About the author:

Dr Richard Flook has worked for both suppliers and consumers of minerals with global companies including, Steetley plc, Anglo American, Commercial Minerals (now Sibelco), Normandy Mining Ltd, Omya AG and Shinagawa Refractories.

Richard has been CEO, Managing Director & Director of Asian and Australasian companies. He has specialized in new business opportunities including strategic planning, trading, market development and acquisitions in the industrial minerals industry and has been involved in managing and developing mineral operations and businesses in Asia and Australasia.

Richard is a Fellow of the Australasian Institute of Mining & Metallurgy (FAusIMM (CP)), the Australian Institute of Company Directors (GAICD) and the Australian Institute of Energy (FAIE). Richard is a graduate of Sydney University (BSc First Class Honours, PhD) and the University of NSW (Master of Commerce).

Since opening his consulting business in 2014, Richard’s clients have come from five continents.