Silicon-Nitride Speciality Materials for Product and Process Innovation in Semiconductor and Analysis Technology*

Many areas of technology would be unthinkable today without high-performance ceramics on the basis of silicon nitride for the optimisation of structures and processes. They are used, for instance, for reducing wear, increasing process temperatures, avoiding corrosion or cross-contamination to lightweight engineering or reducing accelerated masses. The ongoing demand for miniaturisation and increased performance of silicon-based electronics and semiconductor products have produced more and more pressure during the last decades. To be able to fulfil the requirements, it is a crucial factor for the semiconductor industry to optimise their high-tech raw materials and processes and to get them more efficient and free of cross-contamination effects. During the first steps, the complete semiconductor process chain was analysed to find the origins for cross-contamination. Subsequently, many metal-made components were substituted by art-similar ceramics and glasses.

State-of-the-art

Due to their art-similar chemical composition, silicon-based ceramics and glasses – mainly silicon nitride, silicon carbide and pure silica – offer a high potential to improve the manufacturing processes for silicon precursors, ultrapure silicon and silicon-derived semiconductors.

The crucial factor for the success is the choice of the most convenient material. Therefor it is necessary to determine all important factors for the component and check them against the material property profiles of the available ceramics and glasses. Furthermore, it is important to consider all possible integration and interaction effects within the assembly and the whole system as well.

Gas Pressure Sintered Silicon Nitride (GPSN) offers the highest strength and the best fracture resistance of these three silicon based ceramics and glasses. Consequently, it is used for many components, for which a combination of both high mechanical reliability and protection against cross-contamination is of major interest. Other factors for the use of GPSN materials can be the advantageous tribological behaviour even in dry running operation, the low thermal expansion as well as the high electrical resistance of approx 10^{14} $\Omega\cdot$cm.

In special cases where there is demand for extra high mechanical strength, reliability and absence of residual pores, it is possible to apply a Hot Isostatic Pressed Silicon Nitride (HIPSN) quality.

Due to the excellent chemical resistance of silicon nitride, it is possible to optimise the first manufacturing steps for chemical pre-products like chlorosilanes. For these applications, FCT Ingenieurkeramik (FCT)is able to provide for example modularly constructed pipelines and ball valves (right now up to the size of DN 200) which can be faced by very high torsional moments or pulling loads during operation (Fig. 1).

Keywords
silicon nitride, semiconductor application, ultra-pure silicon, analysis technology, special material grade

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For handling and processing of high purity silicon powder, air classifier wheels or pelletizer rollers (Fig. 2) are made up to a diameter of 350 mm. Here again the combination of proper mechanical aspects, good contact behaviour and wear resistance is very beneficial. Subsequently, the high purity silicon powders are processed in different crystal growing procedures to mono- or multicrystalline blocks (ingots). Typically, β-Si_3N_4 powder is used as a separating agent on the inner side of the quartz crucibles. The quartz crucibles can only be used once in a growing process, therefore the use of crucibles of Si_3N_4 are evaluated, because they can be used several times.

After cutting the ingots down to thin wafers, the great advantages of silicon nitride are obvious: especially for wafer trays and vacuum plates, which are used for polishing, etching, structuring and coating of the wafers, the use of art-similar ceramic plates is essential. Depending on the step of manufacturing and its requirements – or maybe as well the philosophy of the system supplier – SiSiC, GPSN respective HIPSN as well as quartz glass are used. Out of the same materials, inliners for sputtering and coating machinery are made. For lubricant-free and in the same time low-wear mechanical systems like bearings, linear slides, grabbers and handling systems, GPSN/HIPSN materials are in favour due to their high mechanical performance and reliability..

An especially wide field of application for silicon nitride is opened at the final inspection of micro-chips and completed cards. For the therefore used probe cards very thin ceramic substrates in round and rectangular shapes with a thickness of between 170–450 µm (Tab. 1) are required (Fig. 3). Finally, they are prepared with several hundreds or thousands of small laser drilled holes. Inside these holes the probe contacts are introduced afterwards. In order to ensure a proper and sufficient mechanical stability during grinding and laser drilling, HIPSN or uniaxial hot pressed HPSN materials are preferred. These two high-end material grades exhibit the best mechanical properties and are nearly free of smallest defects.

Despite the described abilities of application and optimisation, in many practical cases even the existing high-performing silicon nitride qualities encounter its limits. The high technical pressure of innovation increases the number of RFQs for silicon nitride materials, which are able to offer a wider and changed profile of properties or a special combination of properties in comparison to the established grades. Beside increasing requirements regarding the purity level, special solutions are stipulated which can offer a significant higher thermal conductivity in comparison to the common level of 20–25 W/m·K.

In other cases, customers need a material solution with adjusted thermal expansion coefficient, which fits as good as possible to the thermal expansion of the Si wafers or even to the upcoming SiC wafer technology.

Fig. 1
Si_3N_4 valve ball for chlorosilanes handling and dosing

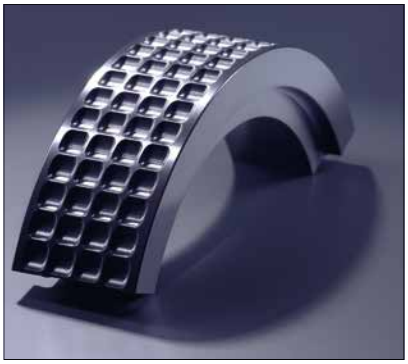

Fig. 2
Si_3N_4 pelletizer roller (cutted segment)

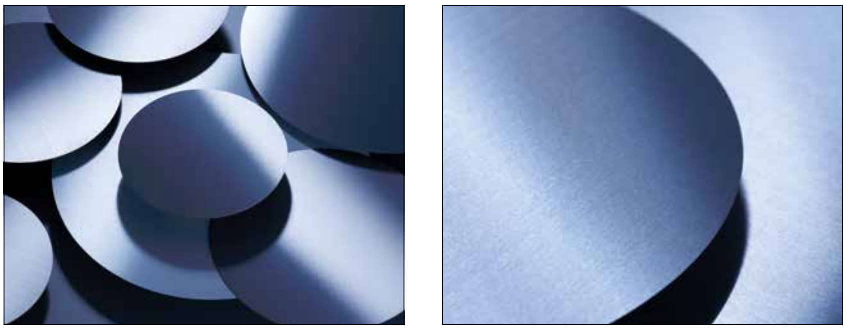

Fig. 3
Si_3N_4 blank plates for wafer chucks and probe cards

Additional application potential by special Si_3N_4 grades

In the last couple of years, research facilities all around the world were investigating and developing new high-end special qualities of silicon-nitride-based materials. Those studies have shown that a notably high potential lies in the optimisation of liquid phase sintered silicon nitride. Through a variation of the used raw materials, sintering additives and processing

Tab. 1
Wafer probe cards: standard blank plates available at FCT

Plate Type	Dimension [mm]	Thickness [µm]			
Square	127 × 127	175	250	320	480
Square	186 × 186	175	250	320	480
Round	∅ 186	175	250	320	480
Round	∅ 205	175	250	320	480

Tab. 2
Silicon nitride materials and their specifications offered by FCT Ingenieurkeramik (measurements: density according to DIN 623-2, four point bending strength and Young's modulus according to DIN EN 843-1, Vickers hardness HV20 according to DIN EN 843-4, fracture toughness calculated via hardness indentation crack length according to Niihara)

FCT Grades / Description	Additives [mass-%]	Density [g/cm³]	Strength [MPa]	Young's Modulus [GPa]	Toughness [MPa√m]	Hardness [GPa]
SN-GP / Standard quality – gas pressure sintered	~10	3,23	670	290	6,5	14,5
SN-HIP / Hot isostatic densified	~8	3,25	880	310	6,2	15,3
SN-PU / Low additive / high purity	~3	3,20	930	320	6,0	15,7
SN-AM / Yttria / rare earth free	<5	3,19	870	310	5,0	15,6
SN-TC / Increased thermal conductivity	<10	3,27	800	300	6,4	15,0
SN-HT / High temperature / creep resistance	<3	3,21	670	310	5,7	15,7
SN-ESC / Electrical semiconductive	~6	3,60	690	325	5,4	15,2
SN-EC / Electrical conductive	<8	4,00	730	340	5,3	14,6
SN-ZO Zirconia containing / Fe-melt resistant	~8	3,50	560	250	6,1	13,7

technologies the properties of the emerging product can be directed exactly in that way it is needed for the later application. However, the transmission of those research findings to the production scale, resulting in tangible products for the customer, proceeds due to technological challenges quite slow.
As a specialist in silicon-nitride-based materials and niche supplier, FCT recognised the sign of the times early on and has therefore been offering specialty Si_3N_4 material variants for several years now. With this wide base of special materials and with its great knowledge in processing those, FCT has the possibilities to deliver high-end products of complex geometries optimised to the customer's specifications. Tab. 2 shows roughly the silicon nitride material qualities offered by FCT.
Besides the standard material grades SN-GP and SN-HIP, the special material grade SN-PU with a remarkable reduced amount of sintering additives and low impurity content is provided. The quality SN-AM is completely free of yttria and other rare earth oxides, while SN-TC provides a much higher thermal conductivity compared to standard grades. On the other hand, SN-HT is a material for high temperature use through the formation of a more creep resistant microstructure. In the field of electrical use, the qualities SN-ESC and SN-EC are no longer isolators – rather they are adjusted to show a semi-conductive respectively conductive behaviour. The materials spectrum is rounded off by SN-ZO, a composite material made from silicon nitride and zirconia with a higher coefficient of thermal expansion, a lower thermal conductivity and an advanced behaviour in contact with iron-containing melts.
In the following passages, some of these special material grades, their property profiles and application potentials especially for semiconductor as well as analysis technology are presented.

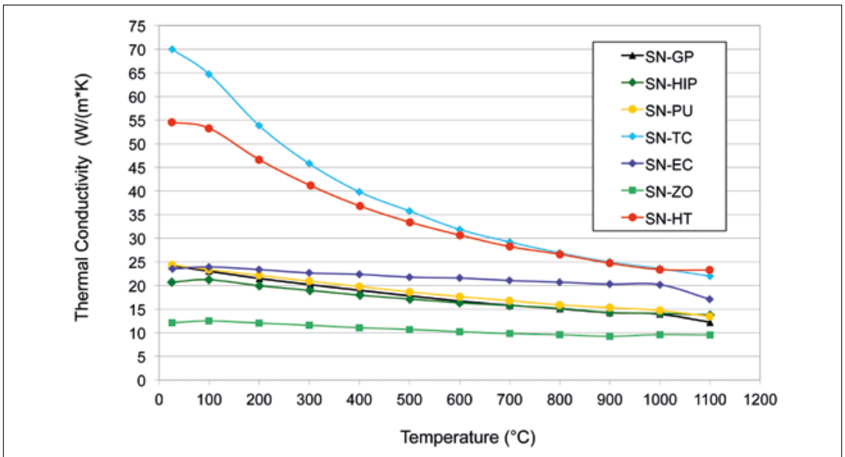

Fig. 4
Temperature-dependent variation of thermal conductivity for different silicon-nitride grades available at FCT

Silicon nitride with reduced amount of sintering additives (FCT SN-PU)

The SN-PU grade was developed at FCT as a special solution for the use in semiconductor technology. Therefore, it was of great interest to reduce process and raw material derived impurities within the material to a minimum.
Additionally, the amount of sinter additives was lowered from typically 8–12 mass-% to about 3 mass-%, yielding in improved material properties. Concerning this, the four point bending strength of 900 MPa surpasses the measured value of the standard quality SN-GP with a remarkable increase of 40 %, while both stiffness and hardness increased at about 10 %, and reach 320 GPa respectively 15,7 GPa. Merely the fracture toughness is lowered from approx 6,5 MPa√m to 6,0 MPa√m.
In the later use, SN-PU shows an improved abrasion resistance and fits therefore per-

fectly for the use in lubrication-free mechanical propulsion systems, linear slides, pelletizer rollers, air classifier wheels or dosing systems for handling of pure silicon powders.

The simultaneously very high stability against corrosion offers potential for the use as chemical resistant liners in structuring, etching and coating equipment. Moreover, the high strength increases the lifetime and the reliability of handling systems, manipulators and grippers.

Targeted substitution of sintering additives (FCT SN-AM)

In some cases within the processing of semiconductors and raw materials, it is not sufficient enough to reduce the impurity level respectively the amount of sinter additives. Instead, it can be necessary to remove certain chemicals respectively elements completely out of the material. Thus, the use of standard silicon nitride grades in hazardous and chlorine containing environments can involve the danger of corrosion effects.

Especially at higher temperatures, the glassy phase between the silicon nitride grains, which nearly always contains yttria, can react with chlorine and form yttrium chloride (YCl_3). The reaction product YCl_3 is then carried away from the reaction zone, because of its high solubility – a passivating respectively a slowing down corrosion layer is not formed.

On the part of FCT a solution also for this specific problem was developed: by the use of the yttria-free respectively rare-earth-free silicon nitride quality SN-AM it is possible to prevent corrosion effects, while the good mechanical strength and the fracture toughness are preserved.

Silicon nitride with enhanced thermal conductivity (FCT SN-TC)

Conventional GPSN materials produced with the standard sinter additive system alumina-yttria typically provide a thermal conductivity between 20–25 W/m·K during room temperature operation.

These conductivities are much lower than laboratory-developed special material solutions, which reach up to 177 W/m·K by optimisation of sintering additives, raw materials as well as manufacturing processes [1]. At this point, FCT's special silicon nitride grade SN-TC gets involved: by change of the sinter additive chemistry

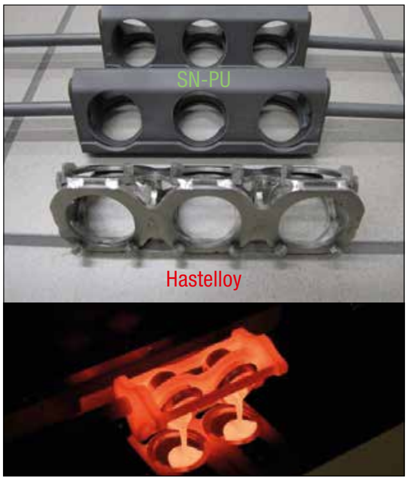

Fig. 5
SN-PU ceramic cradles and holders in borate fusion machines

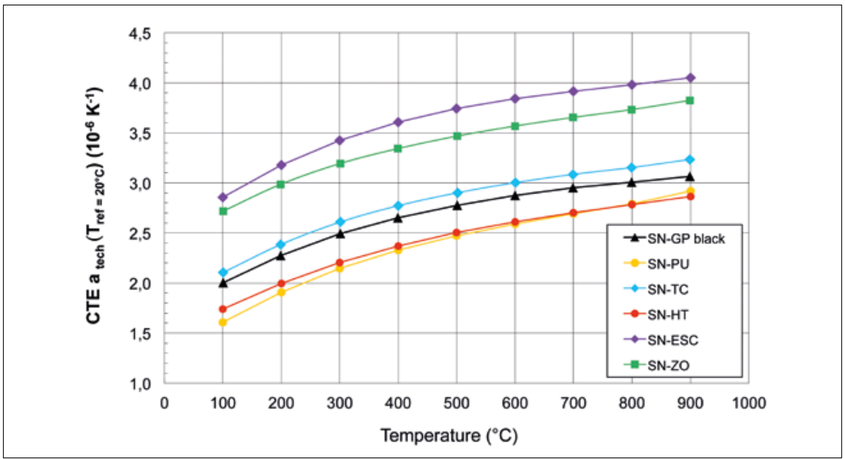

Fig. 6
Variation of thermal expansion coefficient by temperature for different silicon-nitride grades available at FCT (SN-GP and SN-HIP show identical behaviour)

as well as silicon nitride raw materials it was possible for FCT to create a special material grade, which provides a thermal conductivity of approximately 70 W/m·K (Fig. 4).
The lower conductivity of this grade in contrast to laboratory results can be explained in terms of the more usage based approach of FCT to establish a material solution which is suitable for production, and which offers good mechanical performance and an appropriate cost-performance for the customers as well.
Application advantages can be seen for wafer chucks or wafer probe cards, for which the thermal response during heating is much faster and consistent. For precision mirrors, the low thermal expansion in combination with the increased thermal conductivity can improve the optical performance, especially in the case of high local light and radiation intensities, which lead to local heating and thermal expansion effects.
Beside the use for three-dimensional or even large-scaled components, thermal conductive silicon nitride grades are also predestined for high-performance and heavy-duty electronic substrates. Although the material exhibit a lower thermal conductivity in contrast to aluminium nitride, the better thermomechanical properties allow operation with higher and faster cycling of temperature respectively electrical power. For most of these applications, a thermal conductivity of approximately 90 W/m·K is sufficient. However, in many cases of already commercial available Si_3N_4 substrates, the high thermal conductivity was reached at the expense of lower mechanical performance and microstructure, and is only suitable for manufacturing of thin-walled 2D-components respectively.

Special Si_3N_4 grades for analysis technology

However, the application range of FCT's special silicon nitride grades is not limited on the use for semiconductor applications at all – even though it was originally designed with special focus on it. The researches at FCT were quite happy for example, that the special material grade SN-PU with low sinter additive content and higher purity also showed improved corrosion and oxidation resistance – especially during high temperature operation.
Meanwhile, this additional potential is used for borate fusion machines, which are needed for the preparation of X-ray fluorescence samples. This analysis technique widely used in mineralogy and mining begins with melting of finely ground iron ore, mineral sands or geological samples, which are melted in lithium or sodium borate glass at temperatures up to 1200 °C.
Due to the strong corrosion impact of the borate glass melt, the use of platinum crucibles is essential. But also the cradles and holders in the fusion machines are strongly corroded and can even cross-contaminate the XRF samples. To minimise these corrosion effects, to increase the lifetime and to reduce cross-contamination, cradles originally made of nickel-based superalloys are more and more substituted by FCT SN-PU (Fig. 5).

Outlook

The broad range of special material grades which were developed and introduced by FCT Ingenieurkeramik illustrates the enormous potential created by silicon nitride materials with varied property profiles. Furthermore, this assay shows the additional benefits which can be disclosed for the semiconductor industry. Withal, the potential for further improvement and optimisation works on the available special grades is far from being exhausted.
The technological requirements are increasing steadily with time, especially with the introduction of the EUV lithography and the novel silicon carbide-based wafer technology. This fact is strengthening the trend to tailor silicon nitride materials even more focused towards application and customer demand.
Another possibility is to match the thermal expansion of silicon nitride with ultra-pure silicon (approx 2,6 · 10^{-6}/K at room temperature) or silicon carbide wafers (ca. 2,9 · 10^{-6}/K at room temperature). The existing special material grades offer a good starting point for such a tailoring approach (Fig. 6).
Of course, a similar trend can be observed for silicon carbide based ceramics – also for this family of ceramic materials, FCT Ingenieurkeramik develops special material solutions with tailored property profiles to open new opportunities for applications and components.

Reference

[1] Zhou, Y.; Hyuga, H.; Kusano, D.; Yoshizawa, Y.; Ohji, T.; Hirao, K.: Development of high-thermal-conductivity silicon nitride ceramics. J. of Asian Ceram. Soc. **3** (2015) [3] 221–229