Tailoring the Thermal Expansion Coefficient (CTE) of Silicon Nitride and Silicon Carbide Ceramics

The ongoing demand for miniaturization and increased performance of silicon-based electronics and semiconductor products during the last decades requires more and more precise material solutions.

Tab. 1
Wafer probe cards: blank plate dimensions available at QSIL Ingenieurkeramik

Substrate	Dimension	Time	Thickness				
Type	[mm]	[min]	[µm]				
Square	108 × 108	50	125	175	250	320	480
Square	127 × 127	50	125	175	250	320	480
Square	186 × 186	50	125	175	250	320	480
Round	Ø 186	50	125	175	250	320	480
Round	Ø 205	50	125	175	250	320	480
Round	Ø 350	100	125	175	250	320	480
Round	Ø 400	100	125	175	250	320	480

Introduction

Many areas of technology would be unthinkable today without the use of high-performance non-oxide ceramics. In the last couple of years, investigation and development works focused more and more on special material grades. The variation of chemistry, phase composition, microstructure as well as the addition of secondary phases creates the possibility to design material qualities, which offer property profiles adapted on the demand of specific applications and industries. This allows individual solutions outperforming common approaches to solve technical challenges. In previous contributions, some possibilities and potentials for tailoring silicon nitride towards higher purity, chemical resistance and thermal conductivity [1] as well as electrical modification of silicon carbide ceramics [2] were discussed.

The ongoing demand for miniaturization and increased performance of silicon-based electronics and semiconductor products during the last decades requires more and more precise material solutions. Three important trends within the semiconductor industry can be identified, which make it necessary to take a closer look on the Thermal Expansion Coefficient (CTE) and related mismatch effects:

- Ongoing miniaturization of chip structures, currently reaching 5 nm for mass production (EUV technology)
- Gradually increase of wafer diameters to improve throughput and reduce fabrication costs
- Enlargement of temperature range during probe card testing of wafers and integrated circuits, currently reaching ranges between –40 °C and +200 °C.

Customer-specific tailoring the CTE for silicon nitride ceramics

Since many years, thin plates of high-performance silicon nitride ceramics are manufactured and used for probe cards, which are employed for final inspection of structured wafers, micro-chips and completed cards [1]. The QSIL Ingenieurkeramik provides very thin silicon nitride substrates in round and rectangular shapes with a thickness between 50–480 µm (Tab. 1), with precisely ground or lapped surface. At the customers – manufacturers and specialists for probe cards and testing devices – these plates are prepared with several hundreds or thousands of small laser drilled holes in micron scale. Inside these holes golden probe contacts are introduced afterwards (Fig. 1). Up to the present, high-end HIPSN or uniaxial hot pressed HPSN materials were preferred to ensure a defect-free microstructure for a proper and sufficient mechanical stability during grinding, lapping and laser drilling.

Indeed, it is indispensable to ensure a proper and perfect fit between the contact points of the circuits on the wafer and the probe card contacts. With enlargement of the temperature range for testing, as well as the increase of wafer diameters, serious contacting problems can occur. This makes it necessary to take a thorough and systematic view on thermal expansion, mismatch effects and absolute changes of dimensions and contact positions.

A smart way to overcome mismatch problems between probe card and wafers is to tailor the CTE for the ceramic plates. Because Silicon Nitride ceramics exhibits a quite low thermal expansion ($2,15 \cdot 10^{-6}$/K

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at 150 °C) in relation to silicon wafers, an increase of the CTE has to be reached. Depending on their testing devices, tasks and procedures, customers define individual target-CTE parameters, which are typically located between 3,5–4,5 · 10^{-6}/K for maximum application temperatures in the range of 150–200 °C (compare “target area” in Fig. 2).

Since thermal expansion is an intrinsic effect related on the crystalline structure of the β-silicon nitride material itself, a significant rise of the CTE can only be generated by incorporation of secondary phases with higher thermal expansion. One solution can be the addition of titanium nitride (TiN, CTE 9,4 · 10^{-6}/K at room temperature), as it is done at QSIL for the electrically modified SN-EC material grades (Fig. 2). However, it must be considered that this secondary phase has a quite good electrical conductivity – not suitable for probe cards and electrical testing devices which need isolating surfaces. To ensure a high electrical resistance for probe card applications, a better way is the addition of tetragonal partially stabilized zirconia (TZP, CTE 10,0 · 10^{-6}/K at room temperature).

During first experiments at QSIL, an approach basing on a linear rule of mixture between CTE values was applied to define the volume content of both ceramic phases. However, during CTE testing, deviations between theoretical and measured CTE data were observed. Due to interactions of Zirconia with the oxidic sintering additives used for silicon nitride, lower CTE values were generated than expected. Subsequent readjustment of the zirconia addition resulted in the two composite material grades SN-ZO Type 1146 and Type 1147, which are illustrated in Fig. 2.

During optimisation and tailoring of materials, not only one single parameter is modified. The resulting impact on other material properties and parameters always must be considered thoroughly. At the beginning of QSIL’s material tailoring, there was one quite optimistic expectation that due to the combination of two high fracture toughness materials, the resulting fracture toughness for the composite material can be even higher than for the basic materials. However, experimental results show, that both mechanical bending strength as well as fracture toughness only reach intermediate values for SN-ZO composite grades (Tab. 2).

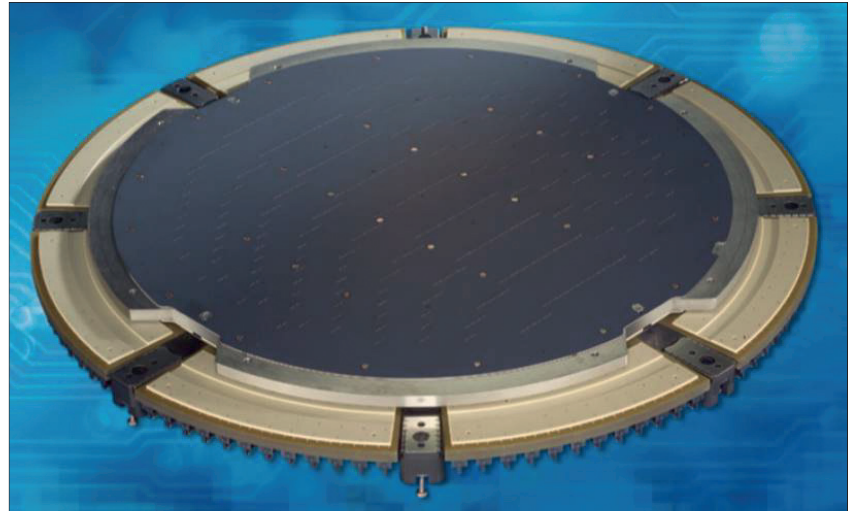

Fig. 1
Wafer probe card made of Silicon Nitride (GPSN)

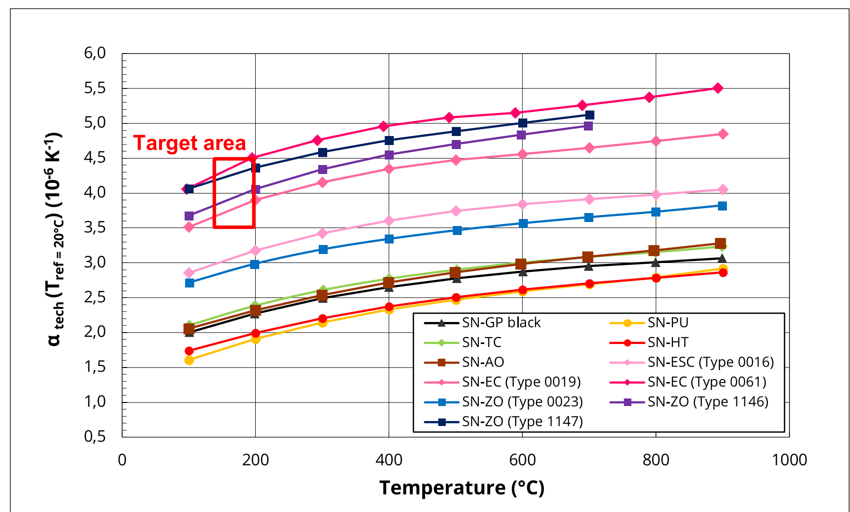

Fig. 2
Variation of thermal expansion coefficient by temperature for different silicon nitride grades available at QSIL-I and CTE target range for probe card applications

The explanation for this behaviour can be found during studying microstructure and strength mechanisms. Both materials are generating their fracture toughness in a different way. While silicon nitride dissipates fracture energy by crack deflection effects, zirconia reaches its high toughness values by stress-activated transformation toughening. However, if both materials are mixed, both microstructural toughening effects are not able to interact with each other in a supporting and multiplying way. SEM microstructural images (Fig. 3) reveal, that crack deflection capability of the silicon nitride phase is quite limited. A similar limitation effect can also be observed for the transformation toughening mechanism, because in the composite material, only a limited volume content of irconia is existing in contrast to the basic material.

For the use for probe card applications, the actual level for bending strength and fracture toughness is sufficient. It can be further improved – but too high expectations on mechanical performance exceeding the required level should be subordinated – otherwise CTE tailoring would be compromised.

For other quite special applications in semiconductor technology, the minim-

Tab. 2 Silicon nitride materials and their specifications offered by QSIL 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)

	Description	Additives	Density	Strength	Young`s Modulus	Toughness	Hardness
		mass-%	g/cm³	MPa	GPa	MPa√m	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 Additve / 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 Semi-Conductive	~6	3,60	690	325	5,4	15,2
SN-EC	Electrical Conductive	<8	4,00	730	340	5,3	14,6
SN-ZO	Silicon Nitride/ Zirconia Composites	~ 6–8	3,50–4,20	560–630	250–290	5,4–6,1	13,7–15,9
SN-AO	Wear Resistant a/ß-SiAlON	~4	3,20	700	300	5,0	18,4

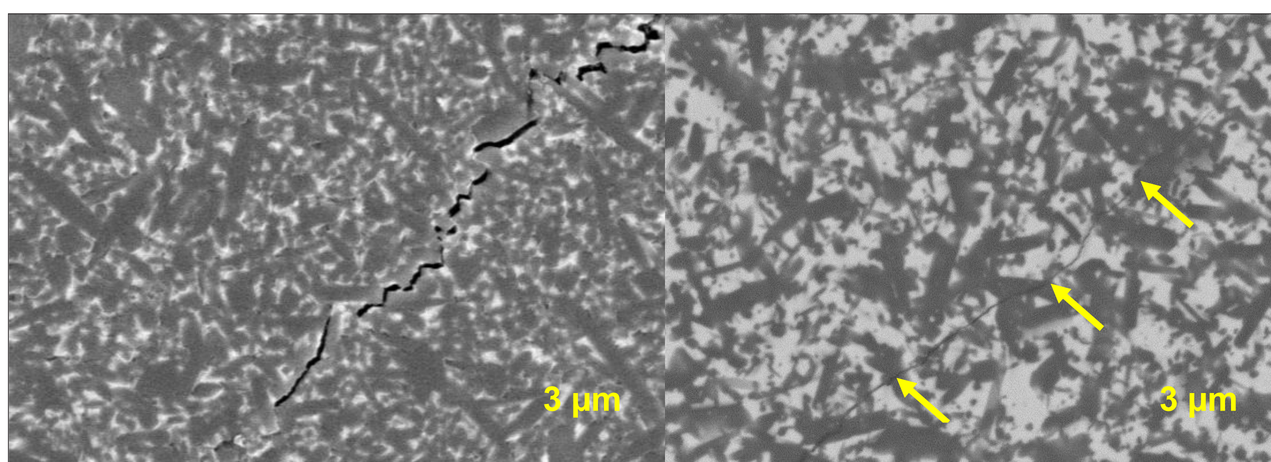

Fig. 3
Comparison of crack morphologies: high fracture toughness silicon nitride (SN-TC) showing strong crack deflection capability (left) vs. silicon nitride – zirconia (SN-ZO Type 1147) with combined crack deflection/transformation toughening behaviour (right)

ization of the CTE for silicon nitride towards ≤ $1,1 \cdot 10^{-6}$/K at room temperature is target of material development. Standard silicon nitride materials (SN-HP or SN-GP) provide a thermal expansion of approx. $1,4 \cdot 10^{-6}$/K at room temperature. Due to the afore-mentioned relation of the CTE on the crystalline structure of the β-silicon nitride material itself, the potential for minimization of the CTE is quite limited. The only way to reach lower CTE values is the systematic minimization of the oxidic sinter additives, which are typically used for liquid phase sintering and densification. While a certain amount of sintering additive is forming the amorphous Si-O-N-based grain boundary phase between β-silicon nitride crystals (thickness in the range of 1–2 nanometres), the remaining excess of oxides a filling pockets and triple points between the crystals. These Si–Y–Al–(Mg)–O–N phases feature higher thermal expansion than the β-silicon nitride phase and increase the overall CTE value of the silicon nitride material. QSIL's special grade SN-HT can overcome this problem: due to an optimized glassy phase chemistry, merely 2,3 mass-% of oxide additives are used – in contrast to approx 10 mass-% used for Standard material grades. This optimization reduces the CTE towards a minimum value of $1,2 \cdot 10^{-6}$/K at room temperature (Fig. 2). A slightly higher CTE value ($1,3 \cdot 10^{-6}$/K) is reached for SN-PU, an alternative material with approx 3 mass-% sinter additive concentration.

For this "low sintering additive – low CTE" approach, the impact situation on other material parameters and properties is better than for SN-ZO materials. The SN-HT grade provides better bending strength, higher stiffness and more reliable fracture toughness values (Tab. 2). If better mechanical properties are provided, a switch to SN-PU can be considered. However, some disadvantages and limitations must be considered also for these material grades: due to the minimized content of sintering additives, the sintering kinetics are limited. This makes it necessary to increase sintering temperature, dwell time as well as sup-

porting pressure (uniaxial load during hot pressing, or isostatic gas pressure during subsequent HIP post-densification) during sinter processing to reach a dense and defect-free microstructure.

CTE tailoring for silicon carbide ceramics

For silicon carbide ceramics, tailoring of the thermal expansion coefficient is possible in a quite similar way. Also here, significant variations can only be reached by introducing a secondary phase, which offers a differing CTE level. Considering the trend and demand for electrical tailoring of silicon carbide to enhance the use as heating elements or to allow electrical discharge machining, the incorporation of either titanium diboride (TiB_2) or boron carbide/free carbon (B_4C/C) as secondary phases are quite interesting approaches. Fig. 4 shows that higher CTE levels in contrast to standard SSiC (black curve) can be reached by incorporation of titanium diboride (blue curve), while the use of boron carbide/free carbon secondary phases offers the possibility to reduce the CTE values (green graph).

However, for both approaches the impact on electrical as well as chemical and mechanical properties must be considered thoroughly once again. If the volume content of the secondary phase is changed to modify the CTE, this will have a direct impact on the electrical conductivity. Fig. 5 exemplifies the correlation between electrical resistance and the concentration of TiB_2 additions. Consequently, for this class of composite materials the priority for tailoring the CTE and / or the electrical properties have to be considered and defined.

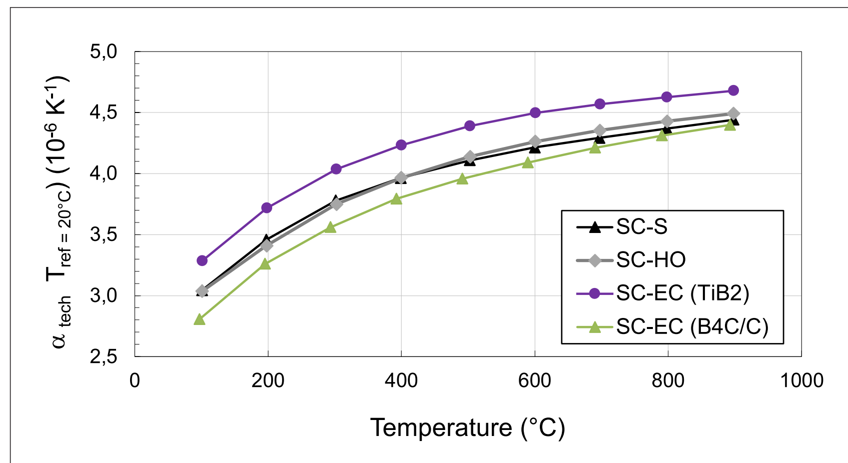

Fig. 4
Variation of thermal expansion coefficient by temperature for different silicon carbide grades available at QSIL-I

Fig. 5
QSIL's SC-EC qualities: influence of titanium diboride (TiB_2) addition on the electrical conductivity

References

[1] Degenhardt, U.: Silicon-nitride speciality materials for product and process innovation in semiconductor and analysis technology. Ceramic Applications **9** (2021) [2]

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