Advances in Parylene Adhesive Bonding for the Realization of Biocompatible Microsystems

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***Abstract* — Wafer to wafer and chip to wafer bonding technologies are a key enabling processes for the fabrication of microsystems. The presented paper focuses on the latest research results of Parylene adhesive bonding. Given the established wafer bonding processes based on Parylene C in vacuum, research on how the bonding process alters the Parylene material was performed using x-ray diffraction. Doing so, a significant increase of the crystalline fraction of Parylene was observed. In order to further develop the Parylene bonding beyond its state of the art, new process variants were successfully established with advanced features: Wafer bonding using Parylene C at increased pressure; Wafer bonding using Parylene N and Parylene F, respectively, to address a different bonding temperature range; as well as chip bonding using Parylene C in air.**

Keywords— Wafer bonding, chip bonding, Parylene, polymer, thermal properties, adhesive bonding, packaging, microsystems, MEMS, biocompatible, microfluidics

I. Introduction

Micro-electro-mechanical systems (MEMS) pave the way for current technology trends such as the Internet of Things, Smart Everything or Industry 4.0, which also represents the forecasted growth of the global MEMS market from $ 14.8 billion in 2022 to $ 22.3 billion in 2027. [1] For the fabrication of MEMS as well as of microfluidic systems, reliable and industry compatible bonding processes are crucial. This particularly refers to large and industry standard wafer sizes and short process time.

For the fabrication of advanced microsystems beyond the state of the art, the bonding temperature should be as low as possible to ensure process compatibility with organic materials. At the same time, the usage of biocompatible bonding adhesives is beneficial to enable the fabricated microsystems to be used for medical applications.

Utilizing the outstanding properties of Parylene, within previous studies, Parylene C (Poly[chloro-p-xylylene]) adhesive wafer bonding was established as a bonding process for biocompatible low temperature wafer bonding in industry scale, providing excellent mechanical and thermal stability as well as a good hermeticity of the bonds, and hence, process compatibility with most established microtechnologies. [2,3]

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Considering the established Parylene bonding process, the presented work focuses to provide a better understanding how the bonding conditions alter the material properties of Parylene as well as to extend the process flexibility and establish new variants. This includes wafer bonding at increased pressures in order to realize cavities with an adjustable pressure as well as bonding with Parylene N (Poly[p-xylylene]) and Parylene F (Poly[tetrafluoro-p-xylylene]) instead of Parylene C in order to address different bonding temperature ranges, e.g. to enable the bonding of wafer stacks consisting of more than two wafers.

Furthermore, the development of a Parylene chip bonding process is of high interest to enable bonding when the wafers are already singulated, considering also the fact, that there is no single roadmap for the heterogeneous integration of MEMS sensors to follow. [4]

II. Experimental

A. Impact of the bonding conditions on Parylene C

Previous studies have proven that Parylene C does not get chemically altered during the established wafer bonding in vacuum using FTIR analysis. [2] However, other studies have revealed a dependency of the Young's modulus and the hardness on the thermal budget, which is assumed to be caused by recrystallization of the partially crystalline polymer. [5] Hence, free-standing Parylene C membranes of 5 µm thickness were fabricated according to the process and using the equipement given in the literature [2] and stored under the typical conditions of a bonding process, i.e. 30 min in vacuum at 260 °C, 280 °C, 300 °C, and 320 °C, respectively. Changes in the crystallinity of the membranes were traced by X-ray diffraction. The experiments were performed on a Bruker D8 Advance Diffractometer equipped with a sealed X-ray tube with a Cu anode. In order to emphasize the contribution of the thin membrane, the glancing angle XRD (GAXRD) setup was used. Therefore, the device is equipped with a Ni/C multilayer mirror to create a parallel beam. The secondary beam was detected, after passing through an antiscatter and receiving slit, by a scintillation counter. The diffraction experiment was performed in asymmetrical geometry with a fixed angle of incidence of 2° in the range $5° < 2\theta < 25°$ with a step size of 0.02° and a dwell time of 12 s per step.

B. *Preliminary investigation of the thermal properties of different Parylene types*

In order to identify reasonable parameter ranges for the experiments presented in this paper, preliminary investigations of the thermal properties of the different Parylene types were performed. Doing so and considering their different thermal properties [6], Parylene C, Parylene N and Parylene F were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in oxygen and inert gas (argon) atmosphere. The chemical structures for the three Parylene types are schematically depicted in Fig. 1.

The Parylene samples for the TGA and DSC measurements were received by depositing approximately 10 µm of the respective Parylene type on 150 mm silicon wafers, which were cleaned using standard cleaning. Subsequently, the Parylene was peeled off the wafer using a scalpel. The TGA and DSC measurements, respectively, were performed using an initial mass of 20 mg to 30 mg of each Parylene type. Doing so, the temperature range was set from ambient temperature to 450 °C for Parylene C and from ambient temperature to 600 °C for Parylene N and Parylene F, respectively. The results of the TGA and DSC characterizations are presented in Fig. 2.

C. *Wafer bonding in non-vacuum conditions*

To enable the sealing of adjustable pressures in cavities, wafer bonding at non-vacuum conditions is required. The TGA and DSC measurements presented in Fig. 2 indicate that all Parylene types decompose more rapidly at oxygen atmosphere in comparison to inertgas. Hence, for Parylene adhesive wafer bonding in non-vacuum conditions, inert nitrogen atmosphere was chosen. Furthermore, to enable a comparison with previous Parylene adhesive wafer bonding results [2], Parylene C was used again. Doing so, 5 x 5 mm² Parylene C bonding frames of 200 µm width and 5 µm height were patterned on 150 mm silicon wafers using the process flow given in the literature. [2] The bonding against plain silicon wafers (Si-P-//-Si) as well as against Parylene C coated silicon wafers (Si-P-//-P-Si) was carried out in an EVG-540 bonder (EV Group Europe & Asia/Pacific GmbH, Austria) at 280 °C and 300 °C, respectively, for 10 min and 1200 mbar nitrogen atmosphere. All other bonding parameters as well as the subsequent routine to measure the tensile and shear strengths, respectively, remained as given in the literature using ten chips per bond. [2]

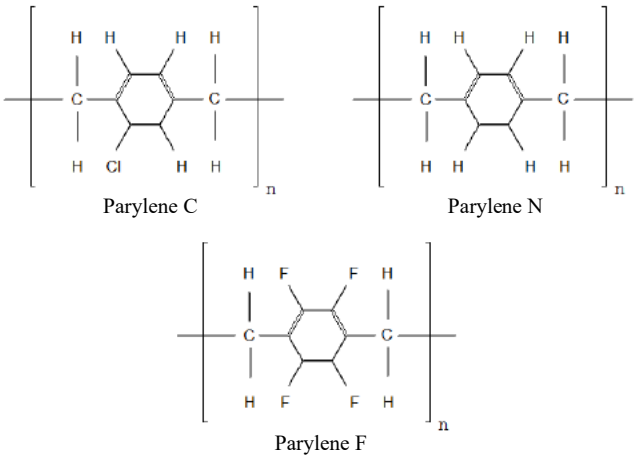

Fig. 1. Chemical structures of Parylene C, Parylene N and Parylene F. [7]

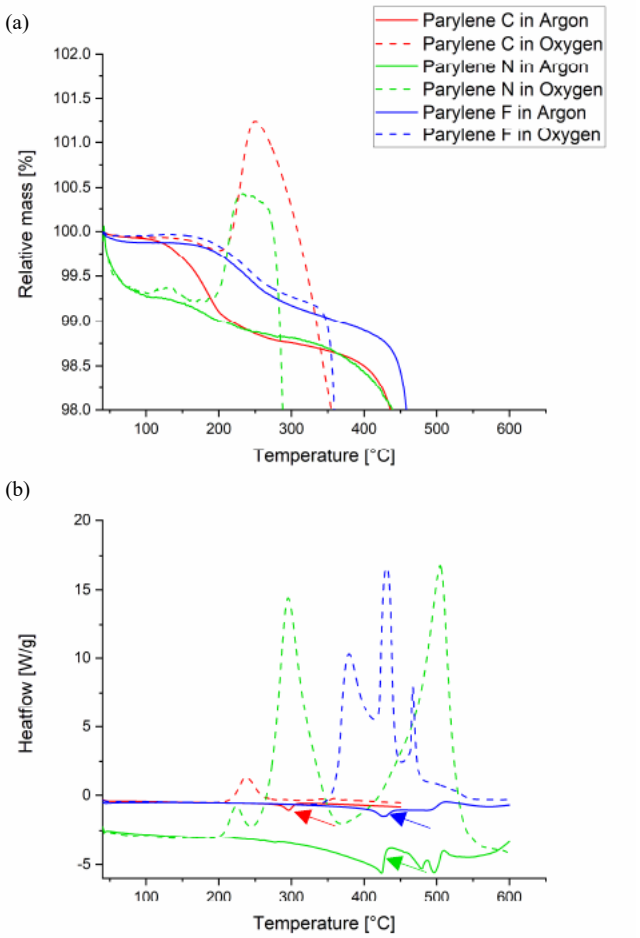

Fig. 2. Results of the TGA (a) and DSC (b) measurements for Parylene C, Parylene N and Parylene F in oxygen and argon. For the DSC results, positive peaks indicate exothermal reactions, whereas negative peaks indicate endothermal reactions. The arrows indicate the melting points of the three different Parylene types in inert gas conditions.

D. *Wafer bonding using Parylene N and Parylene F*

Even though the lower temperature stability of Parylene N reported in literature [6] suggests lower bonding temperatures, previous bonding experiments using Parylene N at temperatures below the bonding temperatures of Parylene C were not successful. [2] Considering the DSC characterization for Parylene C in inert gas, it can be concluded, that typical bonding temperatures in the range of 280 °C to 300 °C are slightly below and above its melting point at 296 °C, which is indicated by a small endothermal peak in the DSC results. Moreover, the DSC measurement results indicate the melting point for both, Parylene N and Parylene F, at 424 °C. Hence, the optimal bonding temperature can be assumed in this temperature range. However, considering the TGA measurements in parallel, Parylene N shows a higher mass loss, which starts in contrast to the other two Parylene types directly when heating the material and is most significant at its melting temperature. Moreover, Parylene N decomposes completely slightly above its melting point. Hence, for using Parylene N for adhesive wafer bonding, maximum temperatures at 420 °C were defined, which were lowered to 360 °C in steps of 20 K. In contrast to this, for Parylene F, a bonding temperature range between 410 °C and 450 °C slightly below and above its melting point was defined, which is in similarity to Parylene C.

For both Parylene types, several bonding experiments were performed in vacuum in an EVG-540 bonder (EV Group Europe & Asia/Pacific GmbH, Austria). The sample preparation using Parylene bonding frames, all remaining bonding parameters as well as the procedure for the measurement of the bonding strengths were repeated as described earlier and in the literature, respectively, using ten chips per bond. [2]

Additionally to the wafer bonding experiments in vacuum and in similarity to the bonding experiments in non-vacuum conditions described in section C for Parylene C, Parylene F was bonded at 430 °C and at a nitrogen pressure of 1200 mbar.

E. Parylene chip bonding

To enable Parylene adhesive chip bonding at ambient conditions, the Parylene type with the lowest melting and bonding temperature, respectively, as well as the lowest sensitivity to oxygen at elevated temperatures is advantageous. Since Parylene C features the lowest bonding temperature and no mass loss at bonding temperature even in oxygen atmosphere, this Parylene type was used for establishing a chip bonding process. Again, the Parylene bonding frames described above were fabricated as given in literature. [2] Before bonding, the wafers with the Parylene bonding frames as well as plain silicon wafers for the bonding partners were diced into 5 x 5 mm² chips. The bonding process was carried out using a Fineplacer femto 2 (Finetech GmbH & Co. KG, Germany). In similarity to Parylene C wafer bonding, the bonding temperature was chosen to be 280 °C and 300 °C, respectively, whereas the bonding time was varied between 30 s, 1 min and 10 min, and the contact pressure was varied between 6.45 N and 3.23 N. After bonding tensile tests were performed as described in literature again using ten chips per bonding parameter set. [2]

III. Results and Discussion

A. Impact of the bonding conditions on Parylene C

The obtained results of the XRD measurements are presented in Fig. 3. The position of the Parylene peaks between 13.88° and 14.18° is in good accordance with the values given in literature. [8] For the Parylene, which faced the bonding conditions, a five to six fold higher signal intensity as well as a smaller full width at half maximum is observed compared to the untreated one. This effect is also

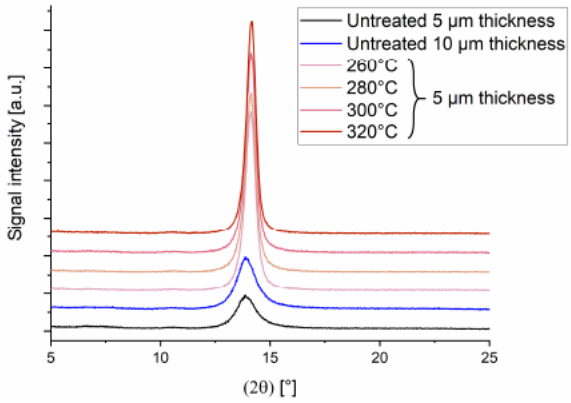

Fig. 3. Results of the XRD measurements of Parylene C annealed at different temperatures in vacuum.

significantly higher than the increase of the signal intensity due to a higher Parylene thickness (1.5 fold when doubling the Parylene thickness). Hence, it can be concluded that the crystallinity of Parylene increases due to the bonding process. According to the literature, it can be assumed that the crystallite size increases. [8] In parallel, the 2θ angle of the peaks slightly increases due to the bonding conditions, which can be correlated to a decrease of the lattice plane spacing. This could possibly be caused by outgassing of volatile components or rearrangement of the structure.

B. Wafer bonding non-vacuum gas conditions

The results for the mechanical strengths of the compounds bonded in inert gas are summarized in Fig. 4 and Table 1. For compounds bonded at 280 °C no difference in the mechanical strengths between bonding in vacuum or nitrogen is observed, whereas for bonding at 300 °C, the compounds bonded in nitrogen show a slightly less mechanical strengths compared to the vacuum bonded ones, but still a higher strengths compared to bonding at 280 °C. Considering that the bonding temperature of 300 °C is above the melting temperature of Parylene C, it can be assumed, that the present nitrogen influences the melting behavior of Parylene C, which leads to decreased bonding strength. This could be also the reason why bonding under nitrogen against Parylene (two bonding partners soften / melt) shows slightly higher mechanical strength compared to bonding against silicon (only one bonding partner softens / melts). Nevertheless, in summary, all bonds in inert gas show good mechanical strengths enabling process compatibility with subsequent wafer processing.

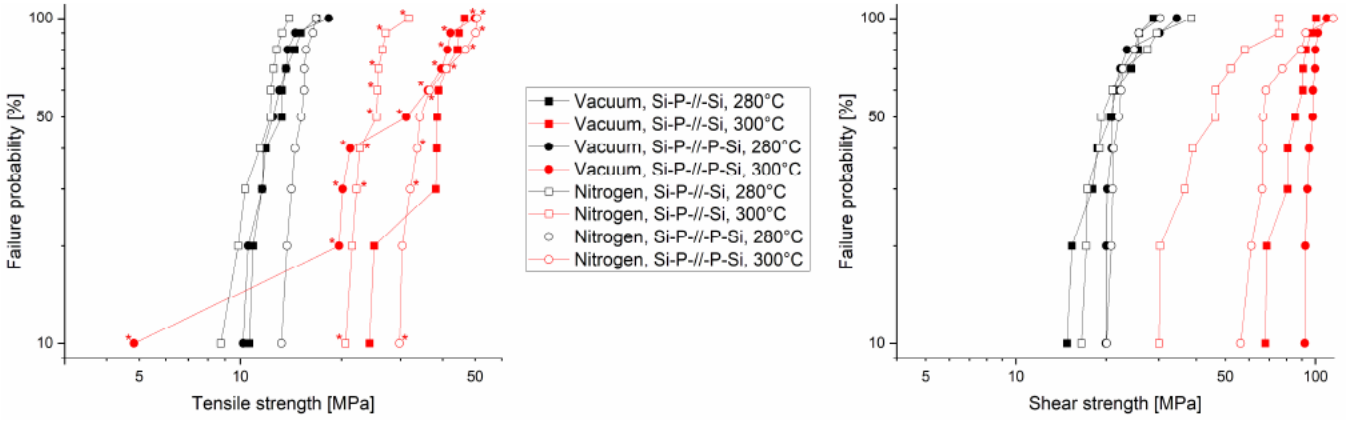

Fig. 4. Tensile and shear strengths of Parylene C based wafer bonding in vacuum and nitrogen, respectively, for bonding against silicon (Si-P-//-Si) and Parylene C (Si-P-//-P-Si). * indicates glue failure between chip and studs.

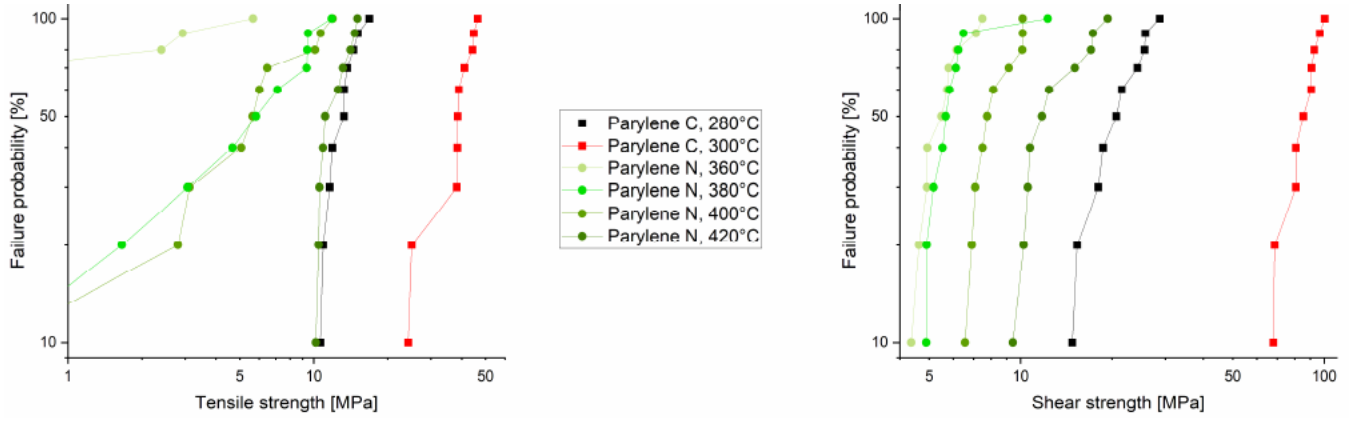

Fig. 5. Tensile and shear strengths of Parylene C and Parylene N based wafer bonding in vacuum. For the values out of the diagram, the pre-force was not reached.

C. *Wafer bonding using Parylene N*

Fig. 5 and Table 1 depict the mechanical strengths for the wafer bonds with Parylene N. The bonding strength shows a strong dependency on the bonding temperature. Even the compounds bonded at 420 °C, i.e. close to the melting point of Parylene N, show only a comparable tensile strength and still a reduced shear strength compared to Parylene C compounds bonded at 280 °C. Considering the cohesive or cohesively/adhesively mixed fraction mechanism of the Parylene N bonds, its reduced tensile strength of only 45 MPa compared to the one of Parylene C with 69 MPa could be a potential reason. [6] However, considering that the tensile strength of Parylene N is about two third compared to Parylene C and the achieved tensile strength of the Parylene N bonds are only about one third of the ones with Parylene C, the bonding parameters seem to have room for further optimization. Since the bonding temperature is limited according to the TGA and DSC measurements, respectively, the bonding time and the contact pressure seem promising parameters for optimization. Nevertheless, the mechanical strengths of the compounds bonded with Parylene N at 420 °C are sufficient to enable process compatibility with subsequent wafer processing. With the established bonding process, Parylene bonding is possible at two different temperature ranges (420 °C for Parylene N and 300 °C for Parylene C), which can be advantageous for the realization of wafer triple stacks. Furthermore, bonding using Parylene N enables Parylene adhesive bonding without halogen containing materials.

D. *Wafer bonding using Parylene F*

The results of the mechanical strengths for Parylene F wafer bonds are depicted in Fig. 6 and Table 1. Again, the bonding strength shows a strong dependency on the bonding temperature, whereas the compounds processed at 410 °C and 450 °C show a lower strength compared to the compounds bonded at 430 °C and 440 °C, respectively. Particularly, the bonding strengths for 410 °C and 450 °C are lower than those of the weaker Parylene C compounds bonded at 280 °C. Doing so, the decreasing bonding strength at lower temperature can be caused due to bonding below the melting temperature of Parylene F. A more detailed analysis of the bonding interface after the mechanical characterizations as depicted in Fig. 7 reveals that at 450 °C the Parylene F becomes so a low viscous liquid that it gets squeezed due to the contact pressure in the bonder. Even though the tensile force and shear force for the compounds bonded at 450 °C are similar compared to those compounds bonded at 430 °C, the increased bond interface by a factor of 3.5 to 4 due to squeezing lowers the bonding strengths as per definition. Since the compounds bonded at 440 °C do not feature reduced bonding strengths or squeezing of Parylene frames, respectively, it can be concluded that the temperature, which reduces the viscosity of Parylene F below a sufficient level, is between 440 °C and 450 °C. Considering the cohesively/adhesively mixed fraction mechanism of the compounds bonded at 430 °C, it can be concluded that this temperature is optimal for adhesive bonding using Parylene F.

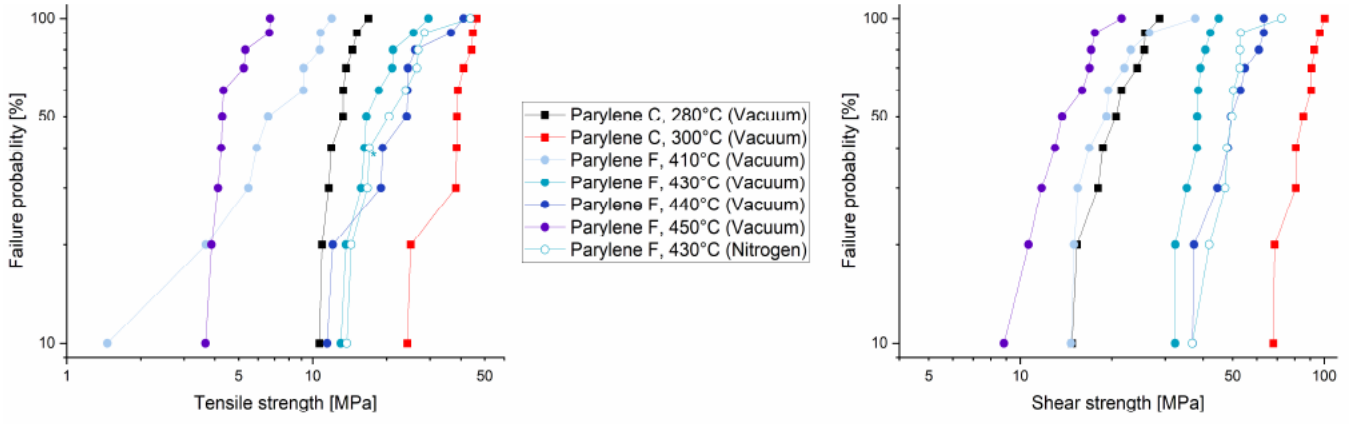

Fig. 6. Tensile and shear strengths of Parylene C and Parylene F based wafer bonding in vacuum and nitrogen. * indicates glue failure between chip and studs.

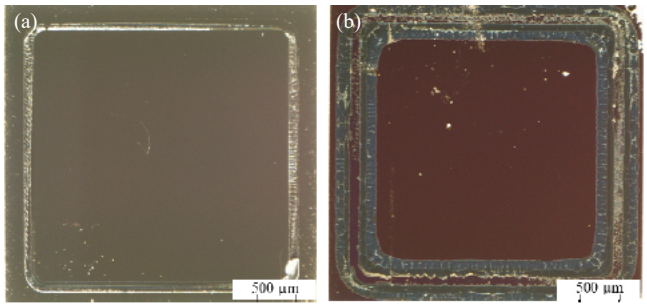

Fig. 7. Parylene F bonding frames after mechanical testing: Compound bonded at 430 °C (a) and 450 °C (b), respectively.

Comparing the results for Parylene F and Parylene C, the bonding strength is in a similar range. Moreover, in similarity to Parylene C, no major difference can be observed between bonding at vacuum conditions or at nitrogen.

In comparison to Parylene N, adhesive bonding using Parylene F has the advantage of higher bonding strengths and less impact of the bonding process on the material itself. Hence, for the realization of triple wafer stacks using two bonding processes at different temperatures, the combination of Parylene F and Parylene C is superior compared to the combination of Parylene N and Parylene C, addressing both the same temperature ranges.

E. Parylene chip bonding

The results for the tensile strengths of the Parylene chip bonds are presented in Fig. 8 and Table 1. Even though the maximum tensile strengths between wafer and chip bonding are comparable for 280 °C and 300 °C, respectively, for the chip bonds, a higher deviation is observed, and hence, the average tensile strengths are reduced. The dependencies of the tensile strengths on the bonding temperature are identical for chip and wafer bonding.

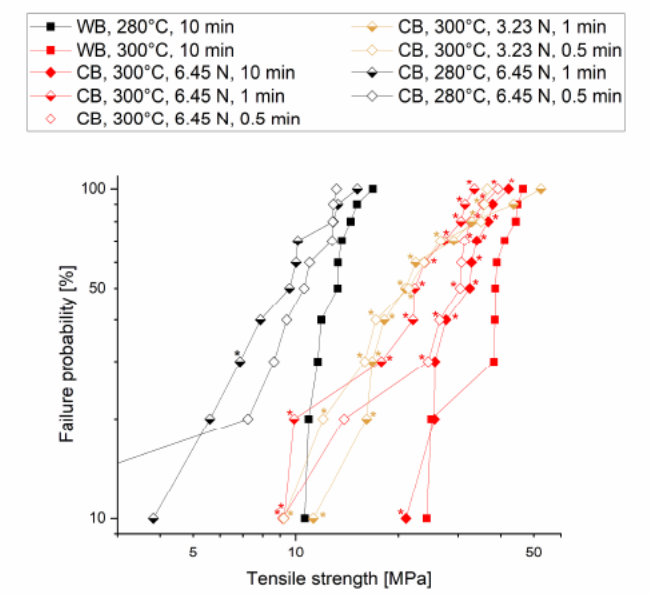

Fig. 8. Tensile strengths of Parylene C based wafer bonding (WB) and chip bonding (CB). * indicates glue failure between chip and studs.

Fig. 8 suggests, that a shortening of bonding time increases the deviation of the tensile strengths, even though it is interesting to note that a bond with only 30 s bonding time is possible. In contrast to this, the tensile strengths are independent on the contact pressure. Considering that the chip bonding is usually one of the last processes of the technology chain, the achieved strengths are sufficient, and hence, a Parylene chip bonding process was successfully established. This process can be advantageous for the bonding of devices such as ultra-thin membranes, which are more sensitive to thermal budgets.

TABLE I. AVERAGE RESULTS AND STANDARD DEVIATIONS FOR THE MECHANICAL STRENGTHS OF THE DIFFERENT PARYLENE ADHESIVE BONDING VARIATIONS (WAFER BONDING (WB) USING PARYLENE C, PARYLENE N AND PARYLENE F IN VACUUM AND IN NITROGEN, VS. CHIP BONDING (CB) USING PARYLENE C IN AIR).

Bonding parameter							Tensile strength [MPa]	Shear strength [MPa]
Bonding type	**Parylene type**	**Partner material**	**Atmos-phere**	**Temper-ature**	**Yield after dicing**	**Remarks**		
WB	C	Silicon	Vacuum	280 °C	100 %	References [2]	13.2 ± 2.0	21.4 ± 4.7
				300 °C	100 %		38.0 ± 7.6	85.5 ± 11.0
		Parylene		280 °C	100 %		13.0 ± 2.3	23.4 ± 4.9
				300 °C	100 %		30.6 ± 13.8	98.0 ± 5.1
WB	C	Silicon	Nitrogen	280 °C	100 %	-	11.8 ± 1.7	22.9 ± 7.1
				300 °C	100 %		24.9 ± 3.3	49.0 ± 16.6
		Parylene		280 °C	100 %		15.1 ± 1.1	23.1 ± 3.1
				300 °C	100 %		38.5 ± 8.1	76.0 ± 17.9
WB	N	Silicon	Vacuum	360 °C	100 %	-	1.1 ± 2.0	5.7 ± 1.0
				380 °C	100 %		6.2 ± 3.9	6.3 ± 2.2
				400 °C	100 %		6.2 ± 3.8	8.4 ± 1.4
				420 °C	100 %		12.3 ± 1.9	13.4 ± 3.5
WB	F	Silicon	Vacuum	410 °C	100 %	-	7.5 ± 3.4	21.0 ± 7.0
				430 °C	100 %		19.1 ± 5.3	38.2 ± 4.0
				440 °C	100 %		23.8 ± 9.4	51.2 ± 9.8
				450 °C	100 %		4.8 ± 1.1	14.7 ± 3.8
			Nitrogen	430 °C	100 %		23.2 ± 9.0	50.5 ± 9.3
CB	C	Silicon	Air	280 °C	N/A	30 s, 6.45 N	9.4 ± 4.0	N/A
				300 °C			27.4 ± 9.4	N/A

IV. Conclusions

The presented work completes existing studies about Parylene C adhesive bonding and proves, that the crystallinity of Parylene C increases significantly during wafer bonding, even though the chemical composition remains unchanged. [2]

Considering the results of a more detailed characterization of the thermal properties of different Parylene types at oxygen and inert atmosphere, new process variants were established successfully. This includes bonding Parylene adhesives at increased pressures using nitrogen atmosphere, at different temperatures range above 410 °C as well as using Parylene N and Parylene F, respectively, instead of Parylene C. Doing so, Parylene F shows superior bonding strengths in comparison to Parylene N. A fourth process variant established successfully within this study is Parylene chip bonding using Parylene C.

The presented process variants enable the realization of cavities with a defined pressure, e.g. for pressure sensors as well as the realization of wafer compounds consisting of more than two wafers. Furthermore, they allow a reliable bonding after the separation of a wafer into chips.

However, for all four process variants, a more detailed analysis is required on how the bonding conditions impact the Parylene adhesive material.

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