Low temperature Si-Si, SiO_2-SiO_2 covalent bonding structures with thin siloxane layer

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Abstract

We present new Si to Si, SiO_2 to SiO_2 bonding technologies for low temperature applications (<200°C). Direct bonding process between Si (or SiO_2) substrates makes high bonding strength without contamination problems. However, high temperature over 1000°C is needed for the reliable Si to Si and SiO_2 to SiO_2 direct bonding processes. To reduce the bonding temperature, thin siloxane layer and low-powered oxygen plasma treatment was used in this study. We used dimethyl siloxane layer having siloxane chains (-Si-O-)n and methyl ends. Siloxane layer is able to be bonded strongly with Si-based substrates at low temperature (<200°C) when oxygen plasma is treated on it. Polymerized siloxane layer such as PDMS has much higher coefficient of thermal expansion (CTE) of 300ppm/K than Si of 2.6ppm/K. When the bonded structure is cooled or heated, the interfaces is possibly distorted and cracked by the high residual stress between siloxane layer and Si substrate. To solve these problems, we developed new fabrications of reducing the siloxane layer thickness to 3~4nm, that is the monomer layer levels. Extremely thin thickness of siloxane layer prevented the problems of the CTE differences. The Si to Si bonding structure with siloxane layer showed strong adhesion properties in this study. The bonded body kept reliable bonding force when it was heated to high temperature (~900°C). The feasible wafer-level bonding process was demonstrated. We investigated the siloxane layer thickness by TEM images. The bonding strength was confirmed by dicing test by 1mm and measured over 20MPa. We also expended this new development to SiO_2 to SiO_2 bonding structures. Low temperature bonding between non-Si substrates such as GaN was possible with thin siloxane layer when amorphous Si thin film was deposited on these substrates.

Key words

dimethyl siloxane layer, low temperature bonding, oxygen plasma treatment, Si- Si and SiO_2-SiO_2 bonding.

I. Introduction

Wafer bonding process has been widely used for the fabrication of micro-electromechanical systems (MEMS) integrated circuits and 3D integration [1], [2]. This wafer bonding process is also applied to an intermediate step in processes, which include the sacrificial metal layers of low melting temperature during bonding process. These metal layers are finally removed for high temperature reliabilities.

We developed Si to Si, SiO_2 to SiO_2 wafer bonding for the new applications. The bonding temperature are to be lowered (<200°C) and the body have to keep reliable bonding strength when it is heated to high temperature (~900°C). Indirect bonding process with intermediate materials such as polymer adhesives or eutectic metals [3], [4] was considered in advance. However, it has problems of contamination and high temperature weakness. Direct bonding process such as silicon to silicon fusion bonding makes high bonding strengths and hermetic sealing without contaminations but it needs high bonding temperature over 1000°C [5]-[7]. Residual stresses by different thermal expansion coefficients cause wafer cracks, thermal damages, degradations of temperature sensitive devices. Therefore, we suggest the wafer bonding method at low temperature without contaminations in this study. Thin dimethyl siloxane layer of 3~4nm is used to lower the bonding temperature. Si to Si,

SiO_2 to SiO_2 bonding structures with dimethyl siloxane layer have reliable bonding strengths. Because the siloxane layer thickness is extremely thin, the bonded body keeps high bonding strength if it is annealed to high temperature.

II. Structure design

Direct bonding technique of Si to Si, SiO_2 to SiO_2 provides reliable bonding strength and clean condition but it requires high bonding temperature over 1000°C. To reduce the bonding temperature, dimethyl siloxane was used in this study. Polymerized dimethyl siloxane layer such as Polydimethylsiloxane (PDMS) is bonded easily to Si or SiO_2 substrate by oxygen plasma treatment [8], [9]. We lowered the bonding temperature under 200°C. PDMS consists mainly of siloxane chains that are alternate structure of silicon and oxygen. Two methyl groups are attached to each silicon atom as shown in Fig. 1(a). When the surface of PDMS film is activated by oxygen plasma, the siloxane chains that make up the backbone of the polymer PDMS are not easily broken, but carbon and hydrogen atoms in methyl groups react with activated oxygen. Dangling bonds are formed on PDMS surface easily by oxygen plasma treatment as shown in Fig. 1(b).

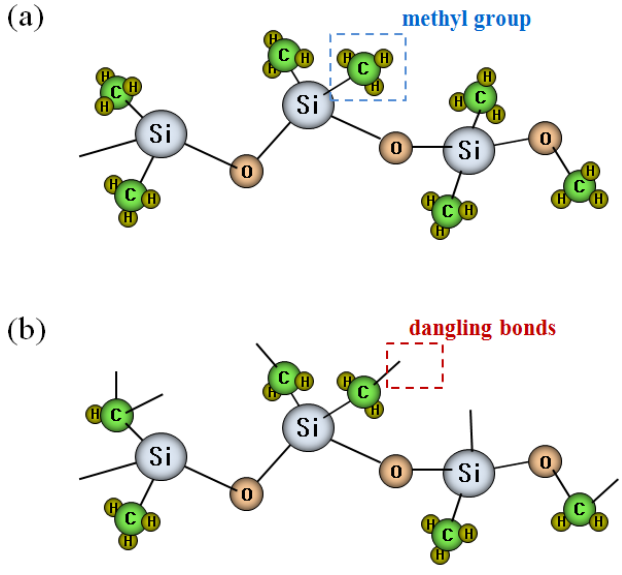

Fig. 1 Polydimethylsiloxane (PDMS) structure (a) before surface oxygen activation (b) after surface oxygen activation

If the activated PDMS surface contacts with Si-based substrates such as Si or SiO_2, the highly activated dangling bonds on PDMS surface formed the covalent bonding with Si-based substrates which have very strong adhesion properties. These dangling bonds make reliable bonding strength even by the room temperature bonding process. The activated PDMS surface reacts with the activated Si surface as follows.

$$\text{-Si-O-CH}_2\text{-} + \text{OH-Si} \rightarrow \text{-Si-O-CH}_2\text{-O-Si} + \text{H}_2\ (g) \quad (1)$$

$$\text{-Si-O-CH}_3 + \text{OH-Si} \rightarrow \text{-Si-O-CH}_2\text{-Si} + \text{H}_2\text{O}\ (g) \quad (2)$$

$$\text{Si} + \text{H}_2\text{O}\ (g) \rightarrow \text{SiO}_2\ (g) + \text{H}_2 \quad (3)$$

PDMS has much higher coefficient of thermal expansion (CTE) of 300ppm/K than Si of 2.6ppm/K and SiO_2 of 0.56ppm/K. The CTE of PDMS is much higher than that of normally used materials in Table 1. Therefore, this structure is cooled or heated after the bonding process, the interfaces is possibly distorted and cracked by the CTE difference between siloxane layer and substrate.

Table 1 Coefficient of linear thermal expansion (CTE) of various materials

CTE (10^{-6}/K)		CTE (10^{-6}/K)	
0.56	Silicon dioxide (SiO_2)	6.5	Tantalum (Ta)
2.6–3.3	Silicon (Si)	4.9–8.2	Chromium (Cr)
3.2	Silicon nitride (Si_3N_4)	8.4–8.6	Titanium (Ti)
4.5–4.6	Tungsten (W)	9.3	Titanium nitride (TiN)
4.8–5.1	Molybdenum (Mo)	13	Nickel (Ni)
6.0	Germanium (Ge)	14	Gold (Au)
6.1	Hafnium (Hf)	19	Silver (Ag)
5.7–7.0	Zirconium (Zr)	330	Polydimethylsiloxane (PDMS)

To reduce the residual stress by CTE difference, we developed thin dimethyl siloxane layer of 3~4nm thickness. Fig. 2(a) shows that thin dimethyl siloxane layer is adhered between Si substrates. Since the thin dimethyl siloxane layer consists of siloxane chains (-Si-O-)n and methyl groups, dangling bonds was easily formed after oxygen plasma treatment. We lowered the process temperature of reliable bonding strength below 200°C. The dangling bonds of the siloxane layer react with Si substrates after oxygen plasma treatment. Due to the extremely thin thickness of dimethyl siloxane, the interfaces distortion and cracks are prevented when the bonded structure are heated. Fig. 2(b) shows that SiO_2 surface also easily react with the thin dimethyl siloxane after oxygen plasma treatment. If amorphous Si film is deposited on non-Si substrate, the strong covalent bonding are formed between the amorphous Si film and thin siloxane layer as shown in Fig. 2(c)

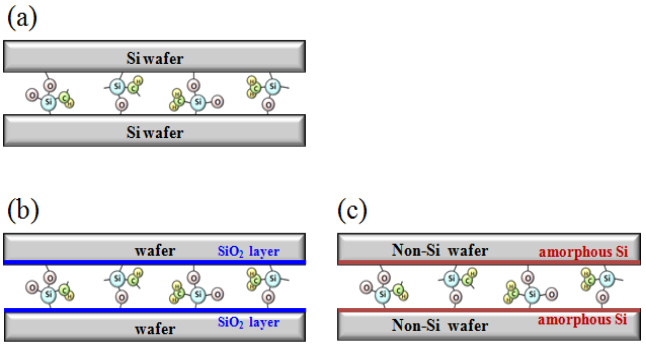

Fig. 2 Si-Si, SiO_2-SiO_2 covalent bonding structures with thin siloxane layer.

III. Wafer bonding process

Commercial prime-grade Si (100) wafers were used for bonding substrates. All wafers are cleaned with organic solvents and H_2SO_4 solutions. Plasma treatment with Ar and O_2 was enhanced on Silicon wafers to form dangling bonds and hydrophilic surface as shown in Fig. 3. Liquid dimethyl siloxane is coated on this activated Si surface. Fig. 4(a) shows that dangling bonds on Si surfaces are bound to liquid dimethyl siloxane during heating at 100°C for 1hour. Most of the liquid dimethyl siloxane remains unbound and easily removed when they are cleaned with organic solvents. Dimethyl siloxane chains of several molecules are bound to such dangling bonds and remained on the surface of Si wafers. These chains become thin adhesive film of 3~4nm thickness. Fig. 4(b) shows that Si wafer with thin dimethyl siloxane are bonded to other Si wafer. Oxygen plasma treatment precedes the bonding process. The oxygen plasma of low RIE power is treated to activate the methyl group of dimethyl siloxane. After oxygen plasma treatment, these activated wafers have to be attached within 1hr, which is important to prevent surface contamination and hold activation effect. Wafer bonding is processed during heating at 100°C for 1hour. To prevent void trapping, bonding processes are to perform in vacuum atmosphere.

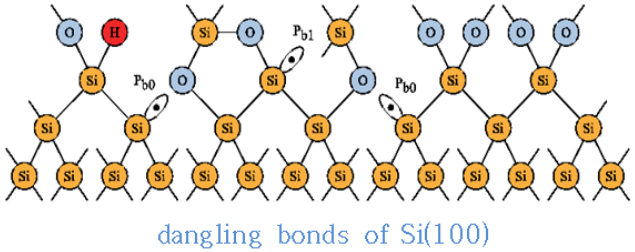

Fig. 3 Silicon surface after plasma treatment

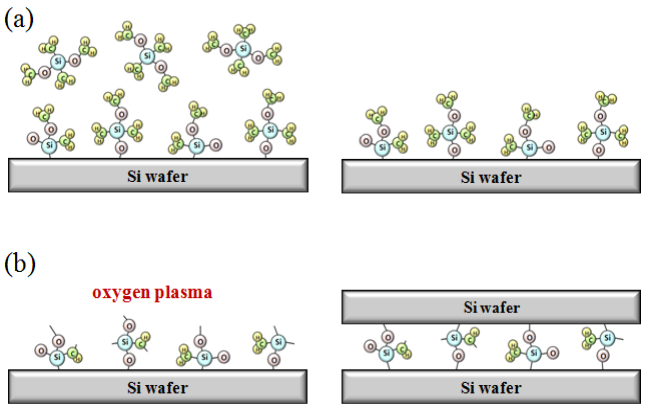

Fig. 4 Wafer bonding process with thin siloxane layer.

IV. Experiment results and discussion

A. Wafer bonding and dicing

Si wafer to Si wafer, amorphous Si to amorphous Si thin film on Si wafer and SiO_2 to SiO_2 thin film on Si wafer were used for wafer bonding experiments with thin siloxane layer in this study. The dimensions of each Si wafer are 150mm diameters and 700µm thickness. Dicing process was done under 2mm/s feed speed. We used nickel dicing blade of 40µm thickness. Fig. 5(a) shows the diced chips of amorphous Si to amorphous Si thin film on Si wafers. All of the diced chips are remained undetached due to reliable bonding strength. We also processed bonding and dicing experiments of Si to Si and SiO_2 to SiO_2 with thin siloxane layers and these wafers also diced into chips without separations.

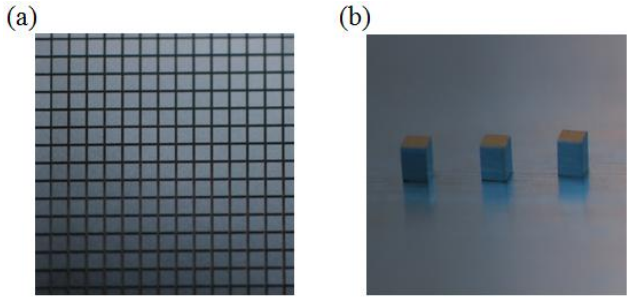

Fig. 5 Diced chips of 0.92mm*0.92mm*1.40mm.

B. Bonding strength

Die shear test was performed to determine the bonding strength. We used the chips of 0.92mm*0.92mm*1.40mm (Fig. 5). The stylus was moved at 0.1mm/s for the shear test. Fig. 6 shows that bonded chips were fractured by two modes after die shear test. Most of the test samples were fractured by mode I. The cracks initiated at the bonded interfaces and

propagated into the bulks. No interface separation was found in mode I. Several samples were fractured by mode II. Some interface separations were found in mode II as shown in Fig. 6(b).

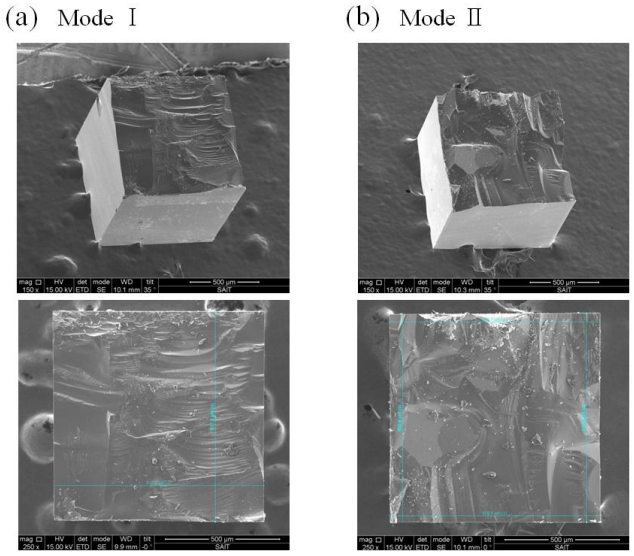

Fig. 6 Facture mode of die shear test

Table 2 shows that shear strengths were measured for Si-Si covalent bonding structures with thin siloxane layer. We used bare Si wafers and amorphous Si thin films on Si wafers. All the measured strengths are more than 12.0MPa that is MIL-STD-883E specification [10] of die shear strengths. Mode I shows slightly higher bonding strengths than mode II.

Table 2 Bonding strength of die shear test (No annealing)

bare Si wafer		amorphous Si layer	
Shear strength (Mpa)	Fracture mode	Shear strength (Mpa)	Fracture mode
20.96	I	30.28	I
23.29	I	29.12	I
29.12	II	36.10	I
20.96	I	29.12	II
24.46	I	29.12	I
29.12	II	26.79	II
29.12	I	25.62	I
32.61	I	39.60	I
29.12	I	33.78	I
26.79	II	32.61	I
30.28	I	31.45	I

The bonding strengths after annealing processes were measured. We annealed the bonded chips at 500°C, 700°C and 900°C for 20min. More than 10 samples were measured for each annealing temperature and the average values of each temperature are shown in Fig. 7. When we measured the samples of the amorphous Si layer after 900°C annealing, the bonding strength is reduced to 15.53MPa. However all the measurements are more than 12.0MPa, MIL-STD-883E specification [10]. Because the siloxane layer has extremely thin thickness, residual stress of the CTE differences is reduced and the bonded body keeps high bonding strength even when it is heated to 900°C.

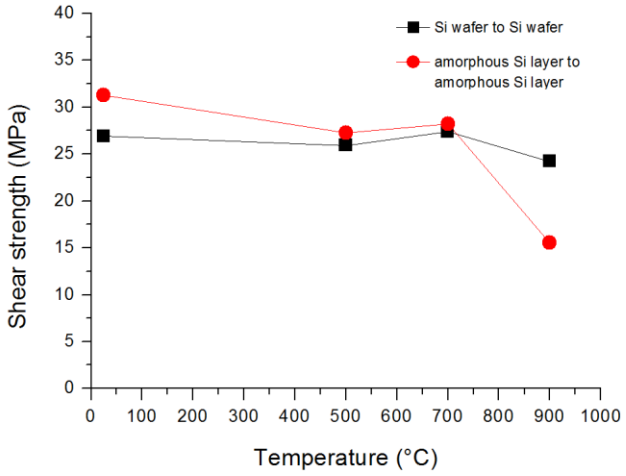

Fig. 7 Bonding strength measurements after annealing process

C. Interface analysis

We had freefall test and broke the wafer to confirm the bonding force and observe the cross section. Si to Si wafer bonding with dimethyl siloxane layer was used in this freefall test. Fig. 8(a) shows the fractured cross section after freefall test. The interface was inspected more closely by TEM as shown in Fig. 8(b). Fig. 8(b) shows SiO_2 to SiO_2 bonding with thin siloxane. We observed the continuous dimethyl siloxane layer of 3nm thickness in Fig. 8(b). Fig. 9(a), 9(b) show amorphous Si to amorphous Si bonding with thin siloxane layer. We also found that the continuous thin dimethyl siloxane layer of 4nm thickness between amorphous Si thin films as shown in Fig. 9. EDX data in Fig. 9(c) represents that thin continuous layer consist of silicon, oxygen and carbon.

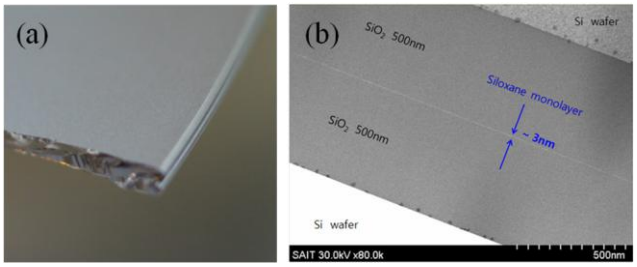

Fig. 8 (a) Cross section of the broken wafer
(b) TEM image of SiO_2 to SiO_2 bonding

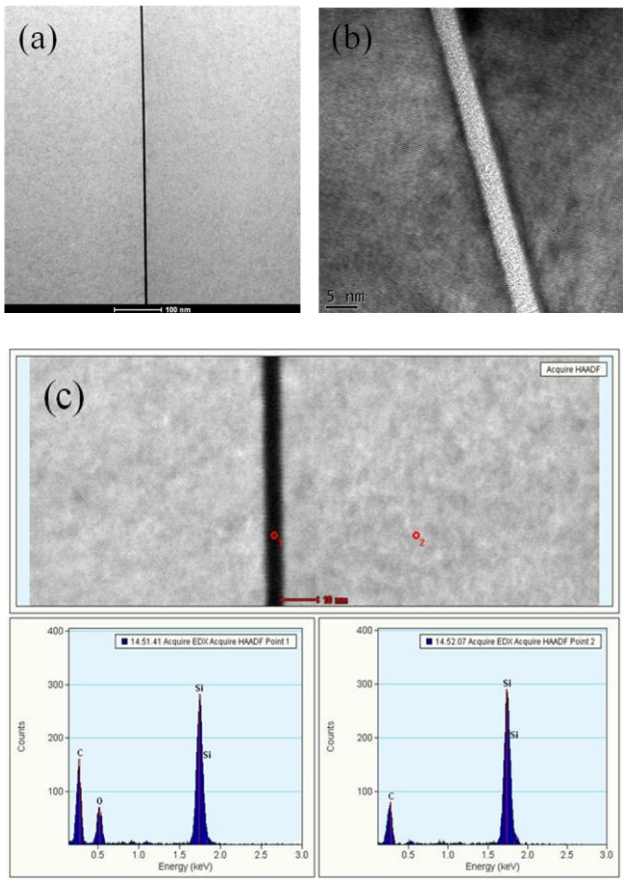

Fig. 9 TEM image of Si to Si bonding

V. Conclusion

We have performed new Si to Si, SiO_2 to SiO_2 bonding processes with thin siloxane layer of 4nm thickness. $Ar+O_2$ and O_2 plasma activation was applied to forming thin siloxane layer and bonding wafers. Amorphous silicon thin films as well as Si substrate was used for Si to Si bonding with thin siloxane layer. To form such a thin siloxane layer, we developed new fabrication method using liquid siloxane and surface activation. We manufactured the Si-Si, SiO_2 to SiO_2 bonding structures at the low temperature below 200°C. These bonded wafers were able to withstand dicing test. All diced chips were remained undetached due to reliable bonding strength. We measured the bonding strengths of Si-Si covalent bonding structures with thin siloxane layer. We used both bare Si wafers and amorphous Si thin films on Si wafers. The measured strengths were more than 20MPa which meet MIL-STD-883E specifications [10] of 12MPa. We annealed the bonded chips at 500°C, 700°C and 900°C for 20min. Bonding strengths were measured over 15MPa after annealing process. Extremely thin thickness of siloxane layer prevented the problems of the CTE difference between Si and dimethyl siloxane. TEM and EDX results show that the continuous dimethyl siloxane layer of 3~4nm are adhered between the surfaces of Si or SiO_2.

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