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ANALYSIS OF THE EFFECT OF HYDROXYL GROUPS IN SILICON DIRECT BONDING USING FT-IR

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규소 기판 접합에 있어서 FT-IR을 이용한 수산화기의 영향에 관한 해석

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Abstract

Silicon direct bonding technology is very attractive for both silicon-on-insulator devices and sensor fabrication because of its thermal stress free structure and stability. The process of SDB includes hydration of silicon wafer and heat treatment in a wet oxidation furnace. After hydration process, hydroxyl groups of silicon wafer were analyzed by using Fourier transformation-infrared spectroscopy. In case of hydrophilic treatment using a (H_2O_2 : H_2SO_4) solution, hydroxyl groups are observed in a broad band around the 3474 cm^{-1} region. However, hydroxyl groups do not appear in case of diluted HF solution. The bonded wafer was etched by using tetramethylammonium hydroxide etchant. The surface of the self etch-stopped silicon dioxide is completely flat, so that it can be used as sensor applications such as pressure, flow and acceleration, etc..

요 약

Silicon direct bonding 기술은 잔류 응력이 없고, 안정한 특성을 가진 센서의 제작과 silicon-on-insulator 소자의 제조에 널리 이용되고 있다. SDB의 공정 절차는 크게 실리콘 웨이퍼의 수산화 공정 과정과 wet oxidation furnace에서 고온의 열처리 공정 과정을 거치게 된다. 수산화 공정을 행한 후, Fourier transformation-infrared spectroscopy를 사용하여 실리콘 웨이퍼 표면을 분석하여 보면, 실리콘 웨이퍼의 표면에서는 수산화기가 생성됨을 알 수 있다. 실험 결과, H_2O_2 : H_2SO_4 용액을 사용한 친수성 용액 처리의 경우에 있어서는 수산화기가 3474 cm^{-1} 주위의 넓은 영역에서 관찰되었다. 그러나, diluted HF 용액의 경우에 있어서는 수산화기가 관찰되지 않았다. 접합된 실리콘 웨이퍼를 tetramethylammonium hydroxide 식각 용액을 사용하여 식각 공정을 수행하였다. 식각 공정은 자동 식각 중지가 수행되었으며, 식각된 표면은 평탄하고 균일하였다. 그러므로, 이러한 SDB 기술은 우수한 특성을 가진 압력, 유속, 가속도 센서 등과 같은 센서의 제작 및 센서 응용 분야에 이용될 수 있을 것이다

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1. Introduction

Wafer bonding techniques have become one of the important steps in the fabrication of microsensors. These technologies provide a powerful and versatile process for improving performance of microsensors and microactuators. Among the

various wafer bonding techniques, eutectic bonding, electrostatic bonding and low temperature glass bonding have been developed in the fabrication of pressure sensors and other sensors.[1,2] However, the bonding of glass to silicon has a thermal stress due to thermal expansion coefficient differences between glass and silicon. This stress is the major cause of drift of sensors. Eutectic bonding technology has used intermediate materials such as coated glass or eutectic metal to bond silicon chips to silicon substrate. These intermediate materials have caused serious defects and impurity problems.[3]

Silicon direct bonding (SDB) technology does not use intervening materials which have caused defects and impurities. Silicon wafers with or without surface layers of thermally grown silicon dioxide can be used, both sides of silicon wafers have exactly the same thermal, chemical and mechanical properties, there will be no problem caused by thermal stress.

A heat treatment at above 1000℃ is usually required to get high strength bonding in SDB technology. The bonding process includes a high temperature treatment and this process limits the application of this technology to device fabrication. Stress free structure is very attractive for both silicon-on-insulator (SOI) devices and sensor fabrication.

This paper describes experiments on the SDB technology according to the solution of hydration. The formation of hydroxyl (OH) groups on silicon wafer surfaces was analyzed by using Fourier transformation-infrared spectroscopy (FT-IR). The self etch-stop of bonded silicon wafer at the intermediate layer (silicon dioxide) was performed by using tetramethylammonium hydroxide (TMAH) etchant.

2. Experimental Procedure

Bonding experiments were done in the clean room (class 10) and performed using commercially available 4 inch-diameter (100) n-type silicon wafer with single-side polished. The silicon wafers were first degreased and cleaned by standard method.

Silicon dioxide on two silicon wafers was grown thermally with 2000Å thickness which was used self etch-stop layer, and the wafers were cleaned by DI water. After this treatment, a hydroxyl groups were formed on the silicon surface by soaking it in a (H_2O_2 : H_2SO_4 = 1 : 3) solution. Then, the wafer was rinsed in DI water and dried.

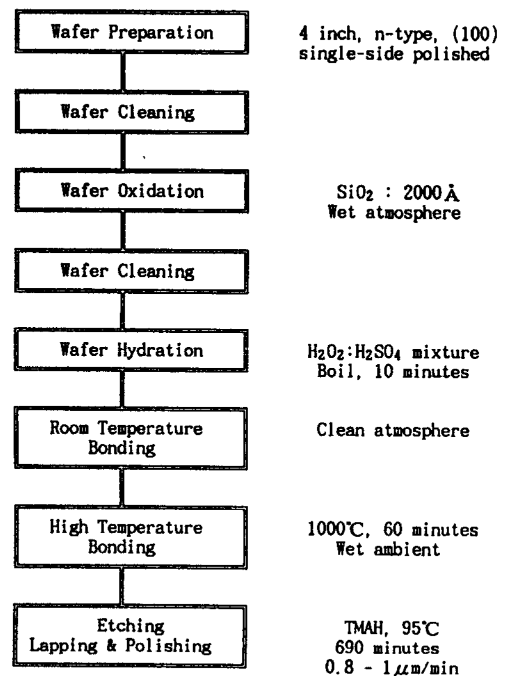

Fig. 1. Experimental procedure of SDB

A pair of mirror-polished silicon surfaces were placed into contact with each other at room temperature in a clean atmosphere. Thermal treatment is necessary to increase the bonding strength. The bonded wafers were put in oxidation furnace at 1000℃, 60 minutes in wet ambient for siloxane bonding.

After the treatment of high temperature, the wafers were lapped, polished and etched by TMAH etchant at 95℃ for 690 minutes. Fig. 1 shows the experimental procedure of SDB.

3. Experimental Results

Precise bonding mechanism is not well known at present. However, it is believed that basic bonding mechanism consists of two steps; the first is silanol bond formation and the second is siloxane bond formation. Fig. 2 shows the above bonding mechanism suggested by researchers.[4,5]

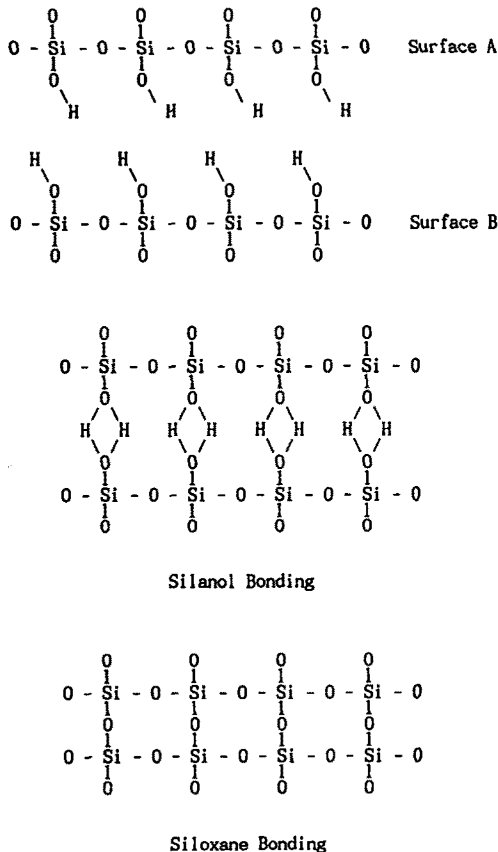

Fig. 2. Bonding mechanism

Hydroxyl groups are absorbed to the silicon atoms chemically. Hydrogen bonds are formed between the hydroxyl groups on the two surfaces. Since the force of silanol bonding is not strong, siloxane bonds are required for a good bonding. As the temperature goes high, the increase of bonding force is made by forming Si-O-Si bonds firmly due to dehydration condensation reaction. A single oxygen bond replaces two hydrogen (H) bonds, the oxygen is covered to silicon dioxide.

In the experiment, the formation of hydroxyl groups was analyzed by using FT-IR (Model: MIDAC FT-IR). The surface of silicon wafer with hydroxyl groups was investigated to obtain information on the surface structure and the reactivity of hydroxyl groups using FT-IR. In general, it is known that a sharp band at 3750 cm^{-1} is universally assigned to "isolated" hydroxyl groups (not hydrogen bonded). A tail, or close-lying band, at 3600 cm^{-1} - 3750 cm^{-1} region appears to be caused by weakly hydrogen bonded with hydroxyl groups. Transmittance centered at 3400 cm^{-1} - 3500 cm^{-1} region is attributed to hydrogen strongly bonded with hydroxyl groups and/or absorbed H_2O. A band at 1030 cm^{-1} - 1090 cm^{-1} region is generally associated with Si-O-Si bonding.[6,7]

Fig. 3 to 6 show variation of hydroxyl groups according to experimental processes using FT-IR. The silicon wafers were thermally oxidized in the oxidation furnace. Fig. 3 shows that silicon wafer surface after cleaning process is analyzed by using FT-IR. A band at 1085 cm^{-1} region is assigned to Si-O-Si bonding of silicon dioxide which is thermally grown, and hydroxyl groups do not appear.

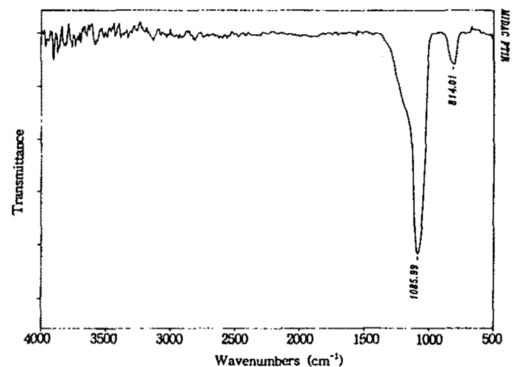

Fig. 3. FT-IR spectrum (after wafer clean process)

The result of wafer hydration using diluted HF

solution and hydrophilic treatment using a (H_2O_2 : H_2SO_4) solution is presented as shown in Fig. 4 and 5 respectively. Fig. 4 indicates that hydrogen bonded with hydroxyl groups do not appear in case of diluted HF solution. However, in case of a (H_2O_2 : H_2SO_4) solution, transmittance at 3474 cm^{-1} region appears, these results show strongly hydrogen bonded with hydroxyl groups in Fig. 5.

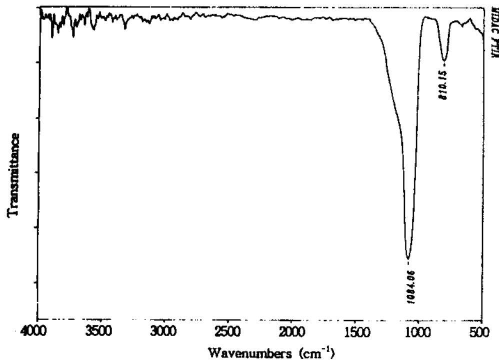

Fig. 4. FT-IR spectrum (after treatment in diluted HF solution)

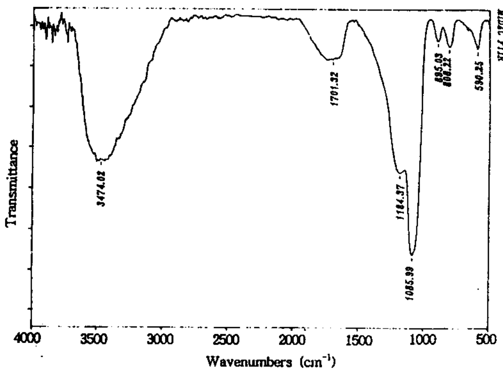

Fig. 5. FT-IR spectrum (after treatment in a H_2O_2 : H_2SO_4 solution)

After room temperature bonding, hydroxyl groups are observed at the broad region around 3524 cm^{-1} as shown in Fig. 6. This indicates that silanol groups are formed on the two silicon dioxide surfaces, and two silicon dioxide surfaces are bonded by polymerization of silanol groups (Si-OH) in the process of room temperature bonding. After high temperature bonding, the band of hydroxyl groups is not observed as shown in Fig. 7, instead a band at 1090 cm^{-1} region is appeared, and this region presents siloxane bonding (Si-O-Si). The main reason is considered that H_2O groups formed on the two silicon wafers are dehydrated during the high temperature process, so siloxane bonding is done.

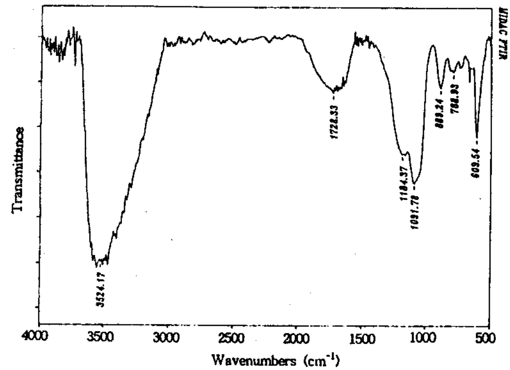

Fig. 6. FT-IR spectrum (after room temperature bonding)

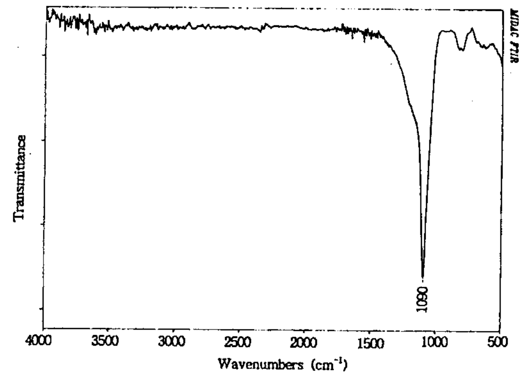

Fig. 7. FT-IR spectrum (after high temperature bonding)

Thermal treatment is performed to increase the bonding strength at 1000℃ for about one hour in wet ambient. The bonded wafer was thinned by a conventional lapping and polishing process and can be observed by infrared viewer or camera. Fig. 8 shows the final void free SDB wafer, but Fig. 9 shows the bonded wafer formed voids. The reason can be considered as follows. During the room

temperature bonding process, the upper wafer is floating on the intermediate air cushion and the attraction often starts simultaneously at different points of the wafer. In this case, the trapped air or gas can cause the void (which is called the first kind of void) and the shape of the void is a circle.[8] This void can be easily reduced by controlled wafer mating. However the attraction starts simultaneously in every point of the wafer surface in most cases.

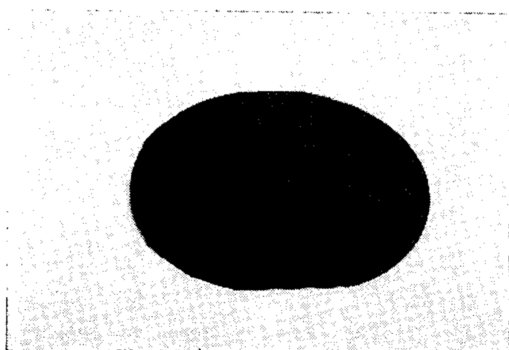

Fig. 8. Photograph of void free SDB wafer

Fig. 9. Photograph of bonded wafer with formed voids

For the treatment of diluted HF solution, the attraction in the room temperature bonding was not strong because of the intermediate air cushion and lack of hydroxyl groups. Even though high temperature process was performed, the bonding strength was not increased and the bonded wafer separated apart easily because siloxane bonding was not formed. However, for the treatment of a (H_2O_2 : H_2SO_4) solution, the attraction in the room temperature bonding was strong relatively because of the hydroxyl groups. After high temperature treatment, the bonding strength becomes bigger.

The second kind of void is due to physical separation of the surface by one or more particles and contaminations and the shape of the void is a circle. This type of void can be reduced by cleaned atmosphere.

The third type of void is caused by physical nonuniformity of the surfaces to be bonded and the shape is an ellipse. This void can be unavoidable because of nonuniformity of wafer.

As the shape of voids becomes a circle in Fig. 9, it is assumed that the voids can be caused by trapped gas or particles and contaminations.

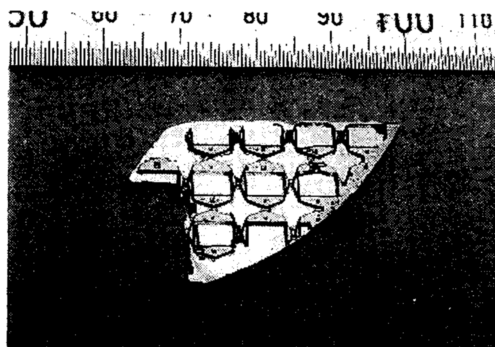

Fig. 10. Backside view of a silicon diaphragm

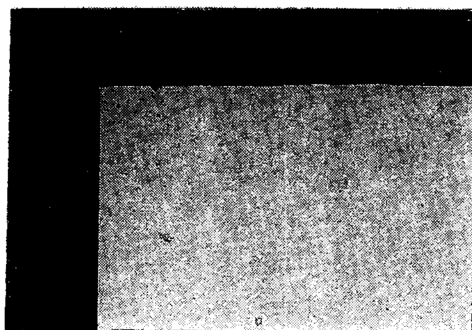

Fig. 11. Image of self etch-stopped SiO_2 surface

Fig. 10 and 11 show the image of the silicon diaphragm that was formed by TMAH selective

anisotropic etching for 690 minutes at 95℃.

Despite of the unpolished initial back-side wafer surface, the surface of the etch-stopped SiO_2 is completely flat and uniform. Among the various methods used to control the thickness of silicon diaphragms, electrochemical p-n junction etch-stop has been used in recent years.[9] However, above all etching methods have quiet complicated and etched surface were not smooth enough. Using self etch stop at the silicon dioxide layer of SDB wafer can simplify etching mechanism and improves the roughness of etched surface.

4. Conclusion

Silicon direct bonding technology is very attractive for SOI devices and sensor fabrication, because of its thermal stress free structure and the stability for both chemical and thermal treatment. As self etch stop is performed, the flat and uniform diaphragm will be easily obtained.

To obtain void free wafer, it is necessary to clean atmosphere which has no particles, contaminations and uniformity of silicon wafer surfaces.

The hydroxyl groups of silicon wafer surface were analyzed by using FT-IR. After the hydrophilic treatment of a (H_2O_2 : H_2SO_4) solution, the hydroxyl groups was occurred in a broad band around the 3474 cm^{-1} region. However, hydroxyl groups do not appear in case of diluted HF solution. When the silicon wafer does not have enough hydroxyl groups, the bonding will not be successful, because silanol bonding is not sufficient.

Even though high temperature process was performed for the treatment of diluted HF solution, the bonding strength was not increased and the bonded wafer separated apart easily. The surface conditions of the silicon wafers to be bonded are also important.

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