

INVESTIGATIONS DURING ANNEALING OF THE INTERFACE IN Si-Si BONDED WAFERS BY MULTIPLE INTERNAL TRANSMISSION INFRARED SPECTROSCOPY

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Multiple Internal Transmission (MIT) technique was used for infrared (IR) spectroscopic investigations during annealing of the interfaces in room temperature Si-Si bonded wafers with different chemical pre-treatments. The evolution with annealing temperature of the chemical species at the interface are used to explain the bonding mechanism of Si wafers in the temperature range of 30-400°C.

1. Introduction

Silicon wafer bonding is an attractive technique to produce silicon-on-insulator (SOI) related microelectromechanical sensors (MEMS) [1,2,3]. Characterisation of the bonded interface in Si-Si bonded wafers is of a paramount importance for improving bonding strength, specially for low temperature wafer bonding processes. Since the bonded interface is buried, classical surface techniques are unable to characterise it. Infrared (IR) spectroscopy is one of the few techniques which can supply valuable information about the chemistry of the bonded interface. In particular Multiple Internal Transmission (MIT) IR spectroscopy was recently successfully employed to study the buried interface in Si-Si bonded wafers [4,5,6].

In this paper we present the results obtained by means of a non-destructive MIT IR two-prisms coupling geometry during annealing of Si-Si bonded wafers prepared using different prebonding procedures.

2. Experimental and measurements procedure

Czochralski-grown (100)-*p*-Si (4 in. diameter, 463µm, 10-40 Ωcm, double side polished) wafers were used for the room temperature (RT) bonding process. In order to achieve hydrophilic Si surfaces different wet chemical treatments and surface plasma

activation were used as presented in Table 1. For each process (RCA, O₂ plasma and RIE) three sets of RT samples were produced. One set of samples was annealed in N₂ for 6h at 200°C and another set was annealed in the same condition at 400°C.

Sample	Pre-treatment
RCA	RCA
O₂ plasma	O ₂ plasma (barrel reactor) + DI water rinsing
RIE	Reactive Ion Etching (RIE) – O ₂ plasma + DI water rinsing

Table 1. Description of the pre-treatments of the Si wafers before room temperature bonding.

The IR spectra were recorded using a dry air-purged Fourier transform infrared spectrometer Bruker IFS66 in the spectral range of 650-4000 cm⁻¹ (HgCdTe detector) with a resolution of 2 cm⁻¹. For all measurements p-polarised light was used and the reference was the empty channel spectrum. The MIT geometry used is schematically presented in the figure 1a. Two prisms made of an IR transparent material (KRS5 or ZnSe) are gently pressed on the surface of the Si wafer in order to get an intimate optical contact. The IR light enters in the Si-Si bonded system via one prism, undergoes multiple internal reflection in the sandwiched structure (the thin bonded interface is tunnelled) and is guided out from the system by the second prism. In this way the IR response of the interface is strongly enhanced due to the manifold interaction of the IR light with the buried interface.

To study the Si-Si bonded wafers we used two MIT configurations:

a) *In situ*. The RT bonded samples were further annealed in a small low-vacuum annealing chamber placed in the air-purge box of the spectrometer. For these MIT measurements ZnSe prisms with an angle of

60° and a distance of 25 mm between the prisms corresponding to 35 passes of the IR light through the interface were used. The spectra were recorded at different temperatures in the range 30°-225°C. With increasing annealing temperature the absorption of IR light by free carrier increases. The spectra measured during annealing are corrected for the carrier absorption by multiplying each spectrum to get the same transmittance level as for RT samples. Nevertheless, for the doping level of the present Si wafers the IR radiation is totally absorbed by free carriers at temperatures higher than 230°C. The MIT configuration we applied should also work at elevated temperatures for samples produced using semi-insulating Si wafers.

b) *Ex situ*. All the samples were measured using a MIT configuration within the air-purge box of the spectrometer. In this case KRS5 prisms with an angle of 62° (providing the same internal angle as ZnSe 60° prisms) were employed and the distance between the prisms was 55 mm which correspond to 77 passes of the IR light through the interface. All MIT IR spectra shown in this paper are normalised with respect to the number of passes.

3. Advantages of the MIT IR with two-coupling prisms geometry

From figure 1b it can be seen that MIT spectra provide complementary information to external transmission (ET) spectra. Using ET valuable information about the structure of the oxide at the interface can be extracted from the region of optical phonons in silicon oxide [7,8]. On the other hand, using ET the chemistry of the interface (region above 1500 cm⁻¹) cannot be studied due to the low sensitivity. The solution for detection of H containing species from the buried interface is to use MIT geometry. Chabal *et al.* [4,5] showed that the ratio between the sensitivity of the MIT geometry and that of the ET geometry for the components of absorbance perpendicular to the interface is enhanced by the following factor:

$$\left(\frac{\Delta I_{MIT}}{\Delta I_{ET}}\right)_{\perp} = N \frac{\sin^2 \theta_{MIT} \cos \theta_{ET}}{\sin^2 \theta_{ET} \cos \theta_{MIT}}$$

where N is the number of passes and θ_{MIT} and θ_{ET} are the internal angles for MIT and ET,

respectively (as plotted in the figure 1a). In this case $\theta_{MIT} \sim 38^\circ$ and considering that $\theta_{ET} = 16.3^\circ$ for external transmission at Brewster angle we obtain an enhancement of perpendicular absorption of ~ 7.5 per pass for MIT compared with the ET geometry. Under these conditions considering the number of passes we obtain that the sensitivity of MIT is larger by more than 2 orders of magnitude compared with the sensitivity of ET for the absorption perpendicular to the interface. This fact provides the reason for using p-polarised light. In the lower spectrum of figure 1b the absorption features of the chemical species at the interface can easily be seen, while the region below 1500 cm⁻¹ becomes practically opaque due to Si multiphonon absorption.

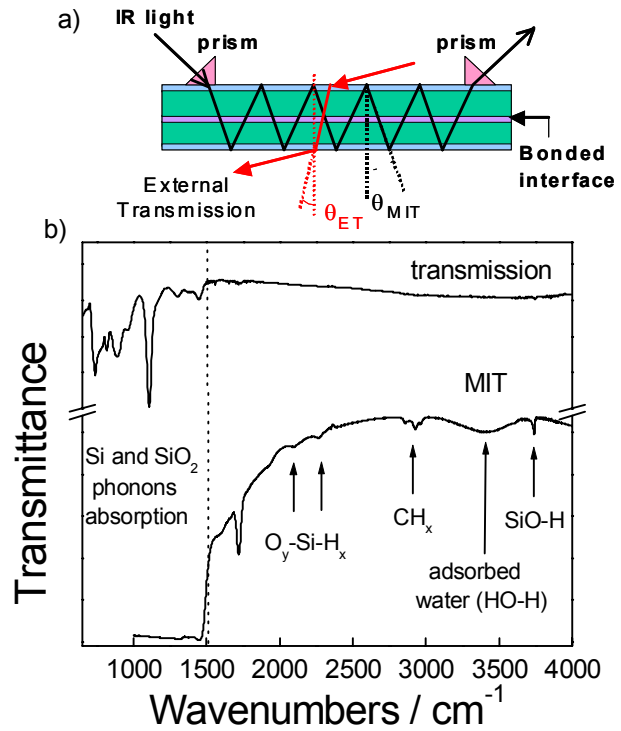


Fig.1 a) Multiple Internal Transmission geometry used to study the bonded interface in Si-Si bonded wafers. The path of the light in the case of external transmission is also plotted; b) IR external transmission spectrum and a typical MIT IR for a Si-Si bonded wafer.

In contrast to the MIT geometry used by Chabal [4,5] which uses cut bevels on the Si-Si bonded wafers the configuration used here does not require additional sample preparation and is thus completely non-destructive. This is advantageous especially for RT bonded wafers where the cutting and polishing of the bevels can induce debonding

of the wafers. Another advantage of our geometry is that the distance between the prisms can easily be varied and in this way different regions of the interface probed by the IR radiation can be studied. Moreover, using prisms with different angles made of different materials (KRS5, ZnSe, Si, Ge) the internal angle θ_{MIT} can be tuned so that the sensitivity ratio $(\Delta I_{MIT}/\Delta I_{ET})_{\perp}$ can be further improved.

4. Results

a) *In situ*. At room temperature bonding of two hydrophilic wafers is realised by the hydrogen bonding between the water molecules adsorbed on the 2 surfaces [1]. The MIT IR spectra for all RT bonded samples (RCA, O₂ plasma, RIE) in figure 2 are dominated by a broad absorption band between 3000-3800 cm⁻¹ corresponding to the stretching vibrations of different hydroxyl groups. The RIE and O₂ plasma samples contain more molecular water (bands centred at ~ 3400-3450 cm⁻¹ at the interface compared to the RCA sample, because the plasma activation produces a more reactive plasma surface able to adsorb more water. During annealing most of the molecular water diffuses away from the

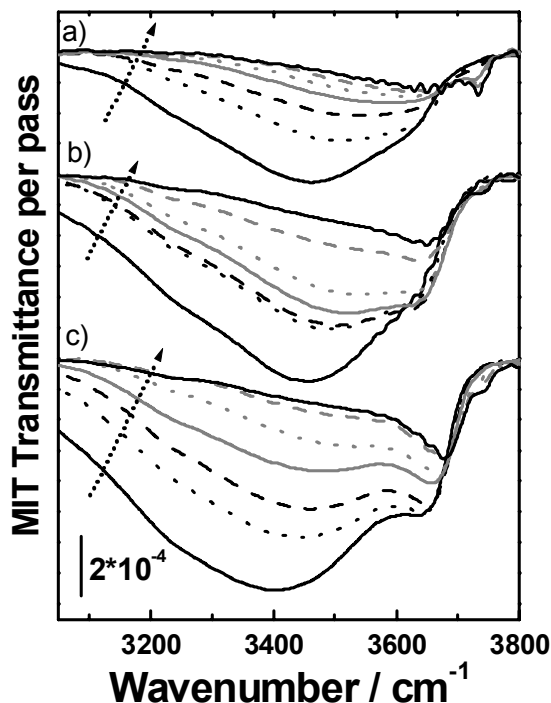


Fig.2 *In situ* MIT IR spectra recorded during annealing in the region of water and SiO-H absorption for a) RCA b) O₂ plasma and c) RIE samples. The temperature increases in the direction of the arrows in the order: 30°, 100°, 125°, 150°, 175°, 200° and 225°C.

bonded interface or into the oxide layer.

With increasing annealing temperature different rearrangements of the water and hydroxyl species take place. For all samples heating induces a reduction in the intensity of the band at 3400 cm⁻¹ suggesting the loss of water at the interface. At 150°C a band centred at 3520-3550 cm⁻¹ corresponding to H stretching vibration of the surface SiOH species which is hydrogen bonded to molecular water [9] can be distinguished. At the same time a band at 3737 cm⁻¹ develops as observed for the RCA sample while in the other two samples a band at 3650 cm⁻¹ (in RIE sample) and a shoulder at the same frequency (in O₂ plasma sample) appear. This means that in the RCA sample isolated (no H bonded) SiOH species are formed while for the other samples the SiOH species are mutually H-bonded [9]. In the case of the RCA sample the isolated SiOH groups do not contribute to the bonding mechanism. For O₂ plasma and RIE treated samples the SiOH groups are H bonded to either vicinal SiOH from the same surface or to SiOH from the opposite surface and are therefore involved in the bonding mechanism of the two silicon wafers. In very good agreement with this statement are the values that are obtained for bonding energies using the blade test method for the samples annealed at 200°C. The measured bonding energies are 1.25 J/m², 1.4 J/m², and 1.9 J/m² for RCA, RIE and O₂ plasma, respectively.

Further increasing of the annealing temperature determine the polymerisation of the SiOH species with formation of siloxane [10] reflected by the decrease of intensity at 3650 cm⁻¹ in all the spectra. When this polymerisation appears between species at opposite surfaces Si-O-Si bridges are formed at the interface contributing to the increasing bonding energy.

b) *Ex situ*. Besides migration away from the interface the water can diffuse into the oxide layer reaching the Si/SiO₂ interface. Here, water dissociates oxidising the surrounding crystalline Si and producing Si-H species [3] or H₂ [10]. Experimental evidence was found for both reactions in the temperature range of 200°-400°C. On the one hand, it can be observed in figure 3 that for the O₂ and RIE treated samples the band corresponding to the stretching vibration of H at Si/SiO₂ interface at

2105 cm^{-1} [11] is increasing in intensity. On the other hand, it is observable for all samples that with increasing bonding temperature the band at 2270 cm^{-1} increases in intensity. This band was attributed to H stretching inside SiO_2 (as O_3SiH groups) [11].

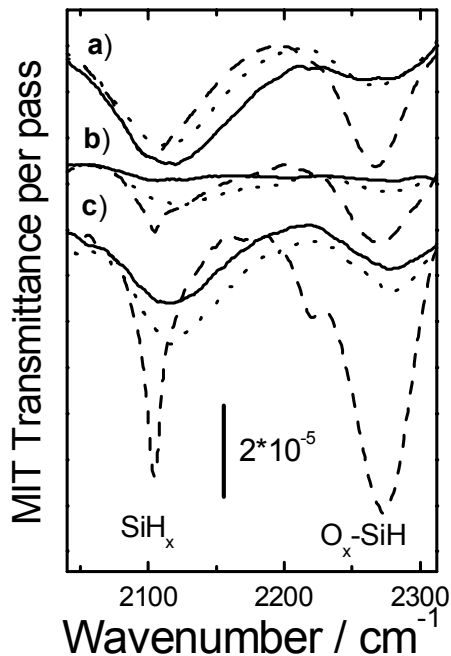


Fig. 3 *Ex situ* MIT IR spectra in the region of $\text{O}_y\text{-Si-H}_x$ vibrations measured at room temperature for a) RCA b) O_2 plasma and c) RIE samples. The spectra correspond to RT prebonded samples (—); 200°C annealed sample (·····); and 400°C annealed samples (- - -).

The H_2 molecules produced by the decomposition of water can diffuse into the silicon oxide interfacial layer producing O_3SiH species. Moreover, it is observed that in the RIE sample with more molecular water at the interface at RT the band at 2270 cm^{-1} at 400°C is stronger compared to the other two samples. For RIE and RCA treated samples having a larger absorption by $\text{O}_y\text{-Si-H}_x$ species at 400°C IR transmission images reveal that small bubbles are formed at the interface at the same temperature. The generation of the interface bubbles can be related to H_2 formed by water dissociation which cannot be dissolved in the thin interfacial oxide [10] and can explain why the O_2 plasma sample showing no bubbles has the largest bonding energy.

4. Summary

A non-destructive two-coupling prisms MIT technique was applied for IR characterisation of bonded interface in Si-Si bonded wafers. The IR spectra were recorded *in situ* during annealing for RT bonded Si-Si samples produced using different chemical pre-treatments of the Si wafers and *ex situ* for 200° and 400°C bonded wafers. The rearrangement of the atoms at the buried interface seen from IR spectra suggest chemical reactions which explain how the bonding of Si wafers is realised.

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