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Sahoo, Hitesh Kumar; Ottaviano, Luisa; Zheng, Yi; Hansen, Ole; Yvind, Kresten

Published in:
Journal of Vacuum Science and Technology. Part B. Microelectronics and Nanometer Structures

Link to article, DOI:
10.1116/1.5005591

Publication date:
2018

Document Version
Peer reviewed version

Citation (APA):
Low temperature bonding of heterogeneous materials using Al₂O₃ as an intermediate layer

Hitesh Kumar Sahoo,¹,a) Luisa Ottaviano,¹ Yi Zheng,¹ Ole Hansen,² and Kresten Yvind¹,b)
¹DTU Fotonik, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
²DTU Nanotech, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

Integration of heterogeneous materials is crucial for many nano-photonics devices. The integration is often achieved by bonding using polymer adhesives or metals. A much better and cleaner option is direct wafer bonding, but the high annealing temperatures required makes it a much less attractive option. Direct wafer bonding relies on a high density of hydroxyl groups on the surfaces, which may be difficult to achieve dependent on the materials. Thus, it is a challenge to design a universal wafer bonding process. However, using an intermediate layer between the bonding surfaces reduces the dependence on the bonding materials and thus the bonding mechanism essentially remains the same. We present a systematic study on the use of Al₂O₃ as an intermediate layer for bonding of heterogeneous materials. The ability to achieve a high hydroxyl group density and well-controlled films makes atomic layer deposited (ALD) Al₂O₃ an excellent choice for the intermediate layer.

We have optimized the bonding process to achieve a high interface energy of 1.7 J/m² for a low temperature annealing of 300 °C. We also demonstrate wafer bonding of InP to SiO₂ on Si and GaAs to sapphire using the Al₂O₃ interlayer.

PACS numbers: Valid PACS appear here
Keywords: heterogeneous materials, direct bonding, Al₂O₃, low temperature, Silicon photonics, laser

I. INTRODUCTION

Direct wafer bonding is a key enabling technology for many current and emerging nanophotonics devices. Most of the work on direct wafer bonding has however been focused on the Si platform for fabrication of silicon-on-insulator (SOI) and micro-electromechanical systems (MEMS). The work on direct wafer bonding of Si to Si/SiO₂ using high temperature annealing from Maszara et al.¹ is one of the earliest efforts on understanding bonding. Tong et al.² furthered the understanding by investigating the contribution of hydroxyl groups and achieved a high interface energy by increased annealing time. These works remain the gold standards for direct bonding. Adapting the bonding process to heterogeneous materials is, however, a challenge. Firstly, high temperature annealing of hetero bonded samples gives rise to thermal stress in the film or even defects due to mismatched coefficients of thermal expansion. For example, annealing of InP bonded to Si at a temperature above 300 °C leads to a build-up of internal stresses in the bonded wafers which creates defects in the InP wafer.³ Integration of heterogeneous materials thus remains one of the roadblocks for semiconductor devices on new platforms such as III-V on Si, Ge on Sapphire, LiNbO₃ on GaAs etc. Secondly, it is important to maximize the density of bond sites, i.e., the hydroxyl group density for a strong bond. A common way to achieve this is to break the surface bonds by O₂ plasma, Ar sputtering, etc. on a wafer followed by a dip in de-ionized (DI) water to re-hydrolyze the surface. This method has a few drawbacks and cannot be adapted to all systems. The process of breaking surface bonds increases surface roughness.⁴,⁵ Also, dipping in water is not desired, especially when you have MEMS and there is a risk of damaging them. In addition, the maximum hydroxyl group density on a wafer surface is an intrinsic property of the material and thus cannot be increased beyond a certain limit for the desired material. Thus, adapting the Si-Si bonding process to a new material platform does not necessarily guarantee an acceptable bond quality. These concerns have generated a strong interest in finding an alternative solution for bonding of heterogeneous materials at low temperature.

The key to achieving a high interface energy at low temperature lies in the choice of a material with high hydroxyl group density and use that material as an intermediate layer for direct bonding. This would increase reliability and reduce dependence on the substrate material for achieving a high interface energy. Al₂O₃ is an excellent choice for an intermediate layer for direct bonding. It has a high hydroxyl group density of around 18 OH/nm², more than 4 times higher than that of Si,⁶,⁷ Al₂O₃ can also be deposited with high accuracy using atomic layer deposition (ALD). The ALD process helps in achieving thickness control at the sub-nm scale and does not add any surface roughness. There has been some reports on Al₂O₃ based bonding being stronger than Si/SiO₂ direct bonding. However, there is a lack of systematic studies to understand the bonding mechanism using Al₂O₃ as the intermediate layer. In this work, we have investigated the contribution of deposition parameters for Al₂O₃, the thickness of Al₂O₃, and annealing conditions to the bond strength. Finally, an optimized process flow for bonding heterogeneous materials is presented; the process can be applied to most material systems.

II. METHODOLOGY

Characterization is important for the ability to quantify a good bond. It can be either a quantitative or qualitative measurement. Common quantitative wafer bond characterization methods include Maszara’s blade test,¹ and micro-chevron test.¹⁴ Despite high reliability of the latter, the Maszara test is the most used method,¹⁵-¹⁸ because of its simplicity and ease.

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¹Electronic mail: hikus@fotonik.dtu.dk
b)Electronic mail: kryv@fotonik.dtu.dk
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The basic bonding steps are illustrated in the Figure 1. Two prime grade single crystal (100) 2-inch clean Si wafers with a surface roughness around 0.2 nm were chosen in this experiment. (b) A thin layer of ALD Al$_2$O$_3$ was deposited on both wafers. (c) The wafers were then placed on top of each other for pre-bonding. An additional exposure to water vapor, before the pre-bonding, was done for one experiment run to understand the effect of hydroxyl density and temperature. (d) The wafers were finally annealed at low temperature ($\leq 300$ °C) and with a controlled applied pressure.

The amount of Al$_2$O$_3$ required for use as an intermediate layer for direct bonding is very important. It would be desirable to have as little as possible and at the same time not to compromise on the bond quality. For applications such as bonding for MEMS VCSELs, where ALD Al$_2$O$_3$ would be deposited even on the mechanical structure, it is critical to have as thin a layer as possible in order not to alter the mechanical properties of the structure. On the other hand, the amount of material should not be too small for an effective bond.

To study the amount of Al$_2$O$_3$ required for a good bond, the number of ALD cycles was varied from 25 to 500 cycles ($\sim 2$-50 nm). The minimum number of cycles was chosen as 25 cycles to ensure a uniform deposition$^{25,26}$ on the whole wafer. The upper limit was chosen to be 500 cycles to test bond-ability with a thick layer of Al$_2$O$_3$. Figure 2 shows the interface energy measured for wafers bonded with different thickness of the intermediate material. For all thicknesses be-
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B. Density of (-OH) groups

As mentioned earlier, high hydroxyl group density is responsible for robust bond formation as also highlighted in the literature on low temperature bonding mechanisms. The pre-bond step brings bondable surfaces in close proximity and a weak hydrogen bond is formed between the two surfaces. With annealing, these sites would give way to the formation of Al-O-Al thereby chemically binding the two surfaces. So, the process flow should be optimized for maximizing the hydroxyl group density on the wafer surface. In this case, the ALD deposition process for Al₂O₃ decides the surface chemistry. The process of ALD deposition can be described by the equations 2 and 3:

$$\parallel Al-OH + Al(CH_3)_3(g) \longrightarrow \parallel Al-O-Al(CH_3)_2 + CH_4(g)$$

(2)

$$\parallel Al-CH_3 + H_2O \longrightarrow \parallel Al-OH + CH_4(g)$$

(3)

where || implies the top surface of the wafer.

The first reaction with TMA is irreversible and is not affected by the temperature within the reaction temperature regime. The second step, hydroxylation of the surface is often mentioned without a competing reaction, which is a temperature dependent step and is a reversible reaction (Equation 4). At high temperatures, the hydroxy groups from the surface (∥Al-OH) may react with each other (Equation 4) and thus reduce the number of hydroxy groups on the surface.

$$2\parallel Al-OH \longrightarrow || Al-O-Al || + H_2O(g).$$

(4)

So, to test the effect of the dehydroxylation temperature dependent step, 25 cycles of ALD Al₂O₃ were deposited at different temperatures between 200 °C and 300 °C. In another set of parallel runs, the wafers were unloaded from the ALD chamber and were exposed to water vapor for 30 sec before being brought in contact with each other. This process step was included in an effort to re-hydrolyze the surface. In all the above runs, the wafers were not settled on any heat sink.

Figure 3 shows the interface energy measured for wafers bonded with 2 nm of Al₂O₃ intermediate layer deposited at different ALD temperatures. The first set of runs where the temperature of deposition was the only variable, there is no appreciable difference in the interface energy. Even though a
C. Annealing Parameters

Annealing of bonded samples helps increase the interface energy. There are three important parameters - annealing temperature, applied pressure and annealing duration. With higher annealing temperatures, the interface water molecules become more mobile and lead to a change from hydrogen bonding towards covalent bonds. Applied pressure helps bring the wafer surfaces closer and might contribute to increasing the bond quality. Equally important is the duration of annealing, which roughly translates to the time assigned for the above-mentioned mechanism to happen.

In order to optimize the annealing parameters, the pre-bonded wafers were annealed at 200 °C and 300 °C, with/without applied pressure and the annealing duration was varied from 1 hr to 20 hr. The annealing temperature was limited to 300 °C to be compatible with heterogeneous bonding. The decrease in the interface energy with ALD deposition temperature is expected due to decreased hydroxyl density, the temperature regime for the experiments is most likely too narrow to show any profound effect. The second set of runs which included an added 30 sec exposure to water vapor definitely shows a small increase in interface energy relative to the first set of runs. Furthermore, the interface energy for these runs is independent of the ALD deposition temperature. Thus it can be concluded that while ALD deposition temperature has a direct influence on the hydroxyl group density on the wafers, a short exposure to an atmosphere with high relative humidity will help restore some of the hydroxyl groups. To further improve the process, ALD Al₂O₃ deposited wafers should be put on a metal plate (heat sink) to bring the wafer temperature to room temperature in an atmosphere with 50 % relative humidity (standard clean-room). This should help increase the hydroxyl group density.

D. Optimized process flow

The above-discussed results help in proposing an optimized bonding process using Al₂O₃ as the intermediate layer. Initially, the requirement on cleanliness and surface roughness remain almost the same as that of direct bonding, except there is no need for standard wet cleaning steps (RCA, Piranha, etc). Proper handling should be ensured to minimize contamination. Next, as deduced from Figure 2, the wafers are coated with a thin layer (~ 2 nm) of ALD Al₂O₃, deposited at 200 °C. The wafers are bonded right after unloading from the ALD chamber with no additional activation step. The wafers may, however, be placed on a heat sink for some time to maximize the hydroxyl coverage. Lastly, the wafers are to be annealed at highest permissible temperature with an application of small force for 60 min. The bonded wafers are expected to have a high interface energy of around 1.7 J/m². The annealing time, in particular, can be further optimized to achieve a saturated interface energy as reported in Tong et al. An extended anneal can be used after an initial anneal under pressure. Figure 6 shows the interface energy obtained in this work benchmarked against Si-Si direct bonding with annealing time of 1 hr and 100 hr, respectively. The achieved interface energy
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![Graph showing bond strength vs annealing temperature](image)

FIG. 6: (Color online) Interface energy of Si-Si wafers bonded using Al\(_2\)O\(_3\) as intermediate layer annealed at 300 °C for 1 hr, benchmarked against direct Si-Si bonding annealed for 1 hr (Maszara et al.\(^1\)) and 100 hr (Tong et al.\(^2\)).

was high enough for our requirements (surviving substrate removal and post-processing).

IV. BONDING HETEROGENEOUS MATERIALS

The optimized process flow, mentioned above, was successfully applied to two different hetero wafer systems. A 2 inch InP wafer was bonded to thermal oxide grown on a Si wafer and a 2 inch GaAs wafer was bonded to a sapphire wafer. After the bonding, the III-V substrates were etched away until a stop layer, thus leaving less than a micron of InP or GaAs behind (Figure 7). The ability to survive the etch is used by many experimentalists as a qualitative test for the bonding. The voids visible on the wafers are from particles on the wafers before bonding. In another run, a patterned wafer (~1\(\mu\)m steps of SiO\(_2\) on a Si wafer) was bonded to InP. A cross-sectional image of the cleaved wafer is shown in Figure 8. The wafers have been processed further towards interesting nanophotonic devices. For these wafers, Maszara test could not be performed since the high interface energy made III-V wafers break instead of delamination.

V. CONCLUSIONS

We have investigated and optimized a low temperature bonding process using Al\(_2\)O\(_3\) as an intermediate layer to bond heterogeneous material systems. Al\(_2\)O\(_3\) is an excellent choice for the intermediate layer since it has a high hydroxyl group density. We investigated the contribution of ALD Al\(_2\)O\(_3\) thickness, deposition temperature and annealing parameters in order to achieve a high interface energy. We also avoided wet processing or any separate activation steps. This is quite desirable for bonding wafers with open MEMS structures. An interface energy of 1.7 J/m\(^2\) was achieved for Si-Si bonding using Al\(_2\)O\(_3\) as the intermediate layer after annealing for 1 hr at 300 °C. The value is higher than the saturated interface energy for Si-Si direct bonding after annealing at 300 °C. Lastly, we also demonstrated adaptation of the bonding process to two hetero-material platforms.

The presented bonding process technology is expected to find application in the integration of III-V on Si, Ge on sapphire, LiNbO\(_3\) on GaAs, etc and thus paving the way toward a new family of devices.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support from the Danish Innovation Foundation through the HERON project, the Villum Center of Excellence NATEC and the National Basic Research Foundation center SPOC (DNRF123). Andrey Marchevski and Aurimas Sakanas are acknowledged for providing the image of InP bonded to Si/SiO\(_2\) in Figure 7.

REFERENCES

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FIGURE CAPTIONS

[FIG 1] (Color online) Illustrations of the basic steps for bonding wafers using Al<sub>2</sub>O<sub>3</sub> as an intermediate layer. (a) Two prime grade 2 inch clean Si wafers with surface roughness around 0.2 nm were chosen in this experiment. (b) A thin layer of ALD Al<sub>2</sub>O<sub>3</sub> was deposited on both wafers. (c) The wafers were then placed on top of each other for pre-bonding. An additional exposure to water vapor, before the pre-bonding, was done for one experiment run to understand the effect of hydroxyl density and temperature. (d) The wafers were finally annealed at low temperature (≤ 300 °C) and with a controlled applied pressure.

[FIG 2] (Color online) Interface energy of Si wafers bonded using different thickness of Al<sub>2</sub>O<sub>3</sub> as the intermediate layer. Al<sub>2</sub>O<sub>3</sub> was deposited using ALD at 200 °C. The deposition rate is ~ 1 Å/cycle. The samples were annealed at 300 °C for 60 min. The symbols represent the average interface energy and bars represent the standard deviation in the measurements.

[FIG 3] (Color online) Interface energy of Si wafers bonded using Al<sub>2</sub>O<sub>3</sub>, deposited at different temperatures, with (squares) or without (triangles) a 30 sec H<sub>2</sub>O exposure between unloading of wafers from the chamber and pre-bonding. All the samples were annealed at 300 °C with a force of 2 kN on 2 inch full wafers. The symbols represent the average interface energy and bars represent the standard deviation in the measurements.

[FIG 4] (Color online) Interface energy of Si wafers bonded using Al<sub>2</sub>O<sub>3</sub> as the intermediate layer and annealed at different temperatures with/without application of pressure (15 kN on 2 inch wafer) for 60 min. Increase in temperature increases the interface energy but there is no observed effect of applied pressure during annealing.

[FIG 5] (Color online) Interface energy of Si wafers bonded using Al<sub>2</sub>O<sub>3</sub> deposited at 200 °C as the intermediate layer and annealed at 300 °C for different duration. There was no significant change in the interface energy when annealing time was increased from 1 hr to 20 hr.

[FIG 6] (Color online) Interface energy of Si-Si wafers bonded using Al<sub>2</sub>O<sub>3</sub> as intermediate layer annealed at 300 °C for 1 hr, benchmarked against direct Si-Si bonding annealed for 1 hr (Maszara et al.¹) and 100 hr (Tong et al.²)

[FIG 7] (Color online) Images of 2-inch bonded wafers. (a) InP bonded to SiO<sub>2</sub> on Si and (b) GaAs bonded to Sapphire after a III-V substrate etch process.

[FIG 8] Cross-section SEM image of a bonded interface. Patterned SiO<sub>2</sub> on Si using dry etch was bonded to InP wafer with Al<sub>2</sub>O<sub>3</sub> as the intermediate layer.