

SURFACE TREATMENT OPTIMISATION FOR QUARTZ DIRECT BONDING

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Previously we have presented the feasibility of quartz direct bonding [1]. In this work, our pre-bonding scheme was optimised to get the highest possible hydrophilicity and a particle free surface. Immersion in concentrated HNO_3 at 80°C for 150 min followed by RCA1 ($\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$, 5:1:1) with Megasonic® for ten minutes gave the highest degree of hydrophilicity, the smoothest surface, and a total absence of adhered particles. Quartz wafers bonded after this treatment showed no voids. After annealing at 500°C a large number of voids, probably due to trapped water, were observed at the interface. The voids disappeared when a grid pattern was etched in one of the wafers before bonding.

Single crystalline quartz-to-quartz direct bonding is indispensable for making bimorph crystal resonators (BXR) [2] and true all quartz packages (AQP) [3]. These are resonator applications that increase the frequency stability for crystal oscillators. For BXR, slightly different cuts of quartz are direct bonded to each other to broaden the temperature interval where the resonator is frequency-stable. A true AQP uses quartz as a capsule for quartz resonators, this way frequency shifts due to differences in temperature expansion between the resonator and the capsule are avoided, and problems with stability and ageing of some glue vanish if direct bonding is used. The true AQP may offer the optimum conditions for long-term stability.

Our first successful direct bonding scheme used 10 minutes immersion in 80°C HNO_3 followed by a rinse in deionized water [1]. At that stage, there was always some unbonded area at the interface after the room temperature bonding. Increased time in the nitric acid gave cleaner surfaces and a higher degree of hydrophilicity, making a better bond. It was also obvious that measures to get rid of adhered particles must be taken.

In this work, 1.5 by 1.5 inch AT-cut polished square quartz wafers (Micro Crystal, Grenchen, Switzerland) were used. The wafers were submerged in 80°C HNO_3 (69 vol.-%) for different times, ranging from 10 to 1000 minutes.

The surfaces hydrophilicity was determined by a steam test [4]. For very small contact angles, we could not use conventional contact angle measurements. The steam test is an alternative to conventional contact angle measurements for small contact angles; it's non-destructive, very simple and powerful. The wafer is held over a beaker with hot water. The condensation pattern is observed while steam covers the surface. Then the wafer is removed and the evaporation is observed. Different degree of hydrophilicity will show different interference patterns that can be related to the degree of hydrophilicity. The hydrophilicity increased with increased HNO_3 immersion time, up to in-between 100 and 300 minutes. 150 min was chosen as standard procedure.

Particles seem to be a more severe problem for quartz wafer bonding than for silicon wafer bonding. Quartz particles scraped off the edges of the wafer bond hard to the surface and cannot be removed with standard RCA1, or moved with the AFM tip. We presumed that this is due to electrostatic forces. Particles on the surface were detected in an optical microscope at 1000 times magnification in dark field mode. Ten fields of sight were examined, and the particles were counted. After 100 min in HNO_3 , no particles could be observed. Still, after bonding a few particles made their presence known by creating voids. By employing Megasonic® with RCA1 at 65°C for 10 min, the last particles were ripped off, yielding a perfect room temperature bond. The Megasonic is an ultrasonic bath with very high alternating actuating frequencies, around 400kHz.

Surface roughness was determined by atomic force microscope (NanoscopeII®) using a silicon nitride probe in contact mode. The measurements confirmed that the sequential use of nitric acid and Megasonic® with RCA1 gave the best result (rms 0.7 nm), as compared to the original surface (1.3 nm), only nitric acid treatment (0.9 nm), and only Megasonic® with RCA1 treatment (0.9 nm).

After annealing at 500°C , a large number of voids appeared at the interface. Annealing at higher temperatures, up to 1100°C did not influence the appearance of the voids. Thermal cycling of the wafers showed that they still contained trapped gas. When etching a grid of channels with pitch variation in one of the wafers before bonding, the voids disappeared for areas of 6 by 6 mm and smaller. This suggests that the trapped species have a limited diffusion length.

The quartz surface is hydrophilic after the cleaning process described above, which means that hydroxyl (OH) groups cover the surface. Hence, most probably, the room temperature attraction between quartz surfaces can be attributed to hydrogen bonding between the terminating OH groups, just as in the case of hydrophilic silicon or silicon dioxide surfaces. The chemical reactions that occur during annealing should also be similar to the case of silicon bonding, but there is a fundamental difference. Unlike bare or oxidised silicon, crystalline quartz cannot consume or absorb any water during the annealing. All residual water has to diffuse out of the bond to the edge of the wafers. The problem of temperature-dependent voids in the case of low temperature annealing for silicon wafer bonding [5] have diminished over the years. At the same time, the silicon surface quality has improved significantly due to improved chemical mechanical polishing (CMP). We believe that the bubble formation problem for quartz wafer bonding would lessen with improved polishing techniques.

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