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Preliminary study on surface processing of silica glass by atmosphere inductively coupled plasma for direct bonding

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Abstract

The performance for some optical system strongly depends on bonding quality of multiple optic components. For heterogeneous integration of silica glass, the direct bonding contributes to a high-strength combination without contaminating the bonding interface, but the surface activation induced in vacuum leads to low efficiency and process complexity. Accordingly, surface processing by an atmosphere inductively coupled plasma (ICP) is proposed before direct bonding. The high-energy Ar-O_2 ICP is generated to enhance the hydroxyl radical density and produce good surface hydrophilicity. With ICP irradiation for 10 seconds, the initial surface (contact angle of 41.8°) can be turned super hydrophilic (contact angle $< 3°$) which ensures high bonding strength. After ICP irradiation, the roughness and form accuracy of the silica glass substrate were well maintained. In addition, ICP irradiation can clean the surface to improve the bonding strength of samples. It is shown that ICP irradiation can improve the bond strength without degrading the surface characteristics. Therefore, direct bonding assisted by atmosphere ICP processing shows potential applicability for heterogeneous integration of high-performance optics.

Keywords: Silica glass; atmospheric plasma; direct bonding; hydrophilic surface; heterogeneous integration

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1. Introduction

Silica glass is an attractive material for fabricating wavelength-selective switches (WSS) and other optical systems due to its ideal optical properties, for instance, its high physical rigidity, chemical inertness, high thermal stability, and excellent transparency. Many high-performance and complex optical systems are made by bonding multiple optical components through a process known as heterogeneous integration. The application of optical systems made of silica glass is largely influenced by the quality of the bonding. For example, nanofluids are used in the biomedical field for nanoscale detecting and sensing [1, 2]. Bonding is the last and most critical step in the fabrication of glass nanofluids, which directly determines the success of glass nanofluids manufacturing [3].

Nowadays, bonding techniques can be mainly divided into intermediate bonding and direct bonding. Intermediate bonding involves the utilization of specific metals and adhesives for bonding or facilitating bonding [4]. Unfortunately, intermediate bonding can disrupt device performance due to stress creep and metal ion diffusion [3]. In addition, devices manufactured by intermediate bonding are prone to introduce the surface contamination due to residues of specific metals and adhesives after debonding [5]. On the contrary, direct bonding does not require any additional cement at the interface compared to intermediate bonding, thus avoiding the surface contamination [6]. Direct bonding can also achieve high-strength and permanent joining between silica glass [7, 8]. To date, there have been some reports about

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direct bonding of glass. Work by Funano SI et al. [9] reports a neutral detergent for cleaning glass surface, the activation method used in this study is simple and has a high Si-OH density than other cleaning steps, but the drawback is that it requires up to several hours of processing time. Work by Zhou J et al. [10] reports the modified RCA-1 solution with ammonium hydroxide for direct glass-glass bonding. Although this method can achieve high bonding strength (≈ 7.81 MPa), it requires dangerous chemicals and consumes a processing time of 30 minutes. What’s more, there are some reports of surface activation by dry methods, such as vacuum ultraviolet (VUV) light irradiation [11], O_2 plasma irradiation [9], etc. However, these methods need a vacuum environment, which prevents them from being widely used and increases equipment costs. Therefore, the development of a safer, simpler, and more efficient direct glass-glass bonding method is critical for the application of optical devices and systems.

Herein, we propose a simple and efficient method using high-energy atmospheric Ar-O_2 ICP to activate surface of silica glass before direct bonding. The ultra-high density of radical generated during ICP irradiation modifies the surface of silica glass rapidly, making it easier for hydroxyl groups to attach to the surface. Ultimately, hydrophilic surface (contact angle < 3°) can be obtained in less than 10 s by this method. Additionally, during ICP irradiation, the surface is cleaned while maintaining the roughness and form accuracy of the silica glass surface. This process further enhances the bonding strength by promoting excellent surface conditions. Atmospheric ICP irradiation presents a promising application for achieving highly effective direct bonding of silica glass.

2. Experimental

2.1. ICP setup

The large density of radical in the atmospheric ICP without the expensive vacuum device, ensures a rapid and effortless direct bonding process. The schematic diagram of the atmospheric ICP setup is shown in Fig. 1. The setup consists of a radio frequency (RF) power supply (f = 27.12 MHz), a network matcher, an electric spark igniter, a quartz torch, an induction coil, a sample holder, 3-axis numeric controller (NC) platform, and three gas mass flow controllers. The torch is comprised of an inner and outer quartz tube. The RF power supply, network matcher, and induction coil are specifically engineered to deliver and maximize the desired forward RF power. The electric spark igniter ignites the high flow rate gas, exciting the plasma. Three gas mass flow controllers are utilized to precisely regulate the flow rates of O_2 in the inner tube, Ar in the inner tube, and Ar in the outer tube. The mass flow controllers of Ar and O_2 have different ranges, which is essential for achieving precise control of gas flow rate. The carrier Ar of the inner tube serves the purpose of exciting the plasma, while the cooling Ar of the outer tube is used to cool the inner tube and shield the ambient air [12]. The primary function of O_2 plasma is to eliminate surface contaminants and maintain surface smoothness [13]. The excited Ar-O_2 plasma is shown in Fig. 1(b). The 3-axis NC platform is used to perform a comprehensive surface scan of the sample. The time of ICP irradiation is determined by the scanning speed of the 3-axis NC platform.

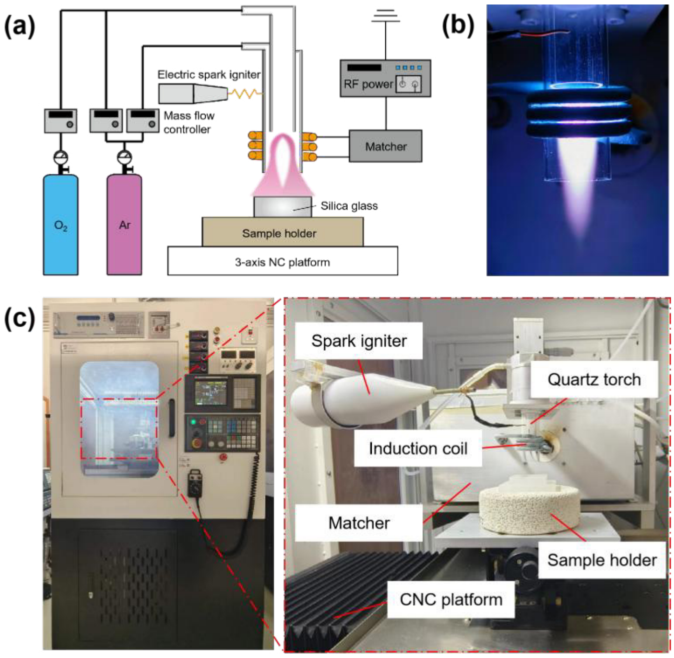

Fig. 1. (a) Schematic of atmospheric ICP setup; (b) Photograph of the Ar-O_2 plasma torch; (c) Photograph of atmospheric ICP setup

2.2. Bonding materials

Double-polished silica glasses (10 mm × 10 mm × 5 mm in size) were used in experiments. The roughness (*S*a < 0.4 nm) and flatness (peak valley (PV) value < 70 nm) of surface meet the surface requirements for direct bonding. Silica glass were rinsed in deionized water with ultrasonic assistance for 3 min before and after ICP irradiation.

2.3. Experimental details

The entire experimental process is carried out at ambient temperature and atmospheric environment. To enhance the surface hydrophilicity of direct bonding, the sample is exposed to an Ar-O_2 plasma with a RF power of 700 W. According to the results of simulations and experiments, the Ar flow rate of the outer and inner torches is determined. Insufficient Ar flow rate in the outer torch hinders effective cooling of the inner torch and fails to shield the surrounding air, resulting in the melting of the inner torch. Conversely, excessive coolant Ar flow rate leads to the intrusion of surplus gas into the plasma's action zone, disrupting the flow field of the inner torch and diluting the concentration of the reaction gas. Similarly, inadequate argon flow rate in the inner torch limits plasma excitation, while excessive flow rate diminishes the effectiveness of the reaction gas. To differentiate the distinct roles of Ar and O_2, two different units of gas flow rate are utilized. In this work, Ar was employed with a flow rate of 1.5 standard liters per minute (slm) for the excitation of plasma, while an additional flow rate of 18 slm was utilized for cooling purposes. However, O_2 flow rate above 80 sccm will result in failure to excite the plasma. Therefore, O_2 is introduced into the process with a maximum flow rate of 60 standard cubic centimeters per minute (sccm). After ICP irradiation, silica glass samples are pre-bonded in a sufficiently humid environment.

2.4. Characterizations

The wettability of the sample surface was analyzed by the contact angle tester (DSA25, KRÜSS). Before and after ICP irradiation, the roughness of the sample surface was evaluated via atomic force microscopy (AFM, Bruker Dimension Edge), while the surface flatness was assessed using laser interferometer (INF150V-LP, TYGGO). Contaminants on the sample surface were detected by the scanning electron microscope (SEM, Gemini 300) and the energy dispersive spectroscopy (EDS, Octane Elite Super, EDAX). The particles present on the sample surface were captured using an optical microscopy (OM, ML15B, Lapsun), and the ImageJ software was utilized to quantify the particle count. The cavity of the bonding interface was observed with a laser scanning confocal microscope (LSCM, VK-X1000, KEYENCE). The surface chemical states were characterized by the X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe III).

3. Results and discussion

3.1. Characterization of surface wettability

ICP irradiation time is a significant parameter for surface wettability. The relationship between the contact angle and the ICP irradiation time was investigated. The contact angle serves as an indicator for assessing the wettability of the sample surface. A surface with greater affinity for hydroxyl groups absorption exhibits higher hydrophilicity, manifested by a significant decrease in contact angle.

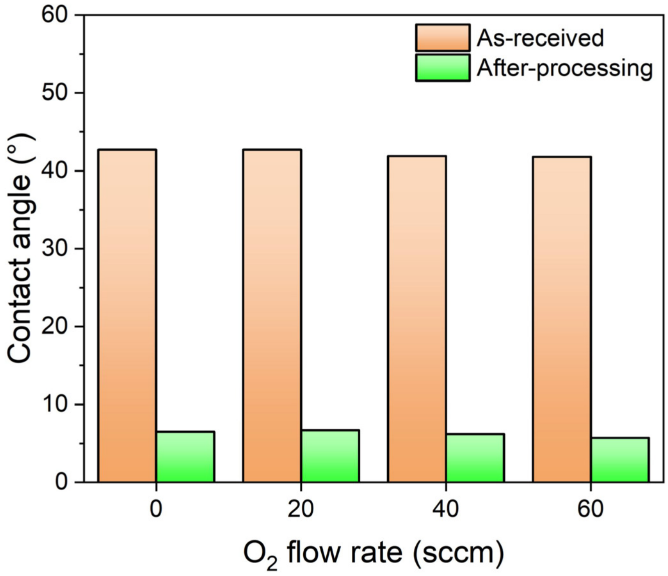

Fig. 2. Relationship between contact angle and O_2 flow rate.

Fig. 2 exhibits the effect of varying O_2 flow rate on the wettability of silica glass surface. After 5 s of processing, the contact angle of the surfaces obtained with different O_2 flow rate are essentially the same. Since the O_2 flow rate used is much smaller than Ar, surface activation is mainly achieved using Ar plasma. In the experiment, O_2 plasma can chemically remove contaminants from the surface. Increasing the O_2 flow rate can effectively enhance the ability of removing contaminants, so subsequent experiments were conducted under the condition of a 60 sccm O_2 flow rate.

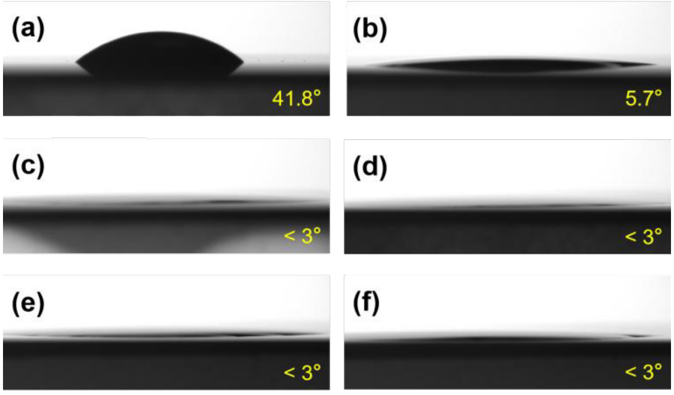

Fig. 3. The contact angle of silica glass under different ICP irradiation time (a) Initial surface; (b) 5 s; (c) 10 s; (d) 15 s; (e) 20 s; (f) 25 s.

The results of silica glass's surface wettability with different ICP irradiation time were shown in Fig. 3. When the sample surface was not activated, the large contact angle indicated that the intensity of the silanol groups on the surface was insufficient for achieving direct bonding. The contact angle of the sample decreased abruptly after ICP irradiation. As the ICP irradiation time increased to 10 s, based on the observation from Fig. 3(c), the contact angle was reduced from 41.8° to less than 3°. The result was evident that the surface displayed a remarkable state of superhydrophilicity. As the irradiation time increasing to 25 s, the surface remains its superhydrophilic properties.

3.2. Characterization of surface flatness and roughness

Direct bonding desires extremely stringent surface conditions, especially surface flatness and roughness. The surface conditions are provided by precision grinding and ultra-precision polishing.

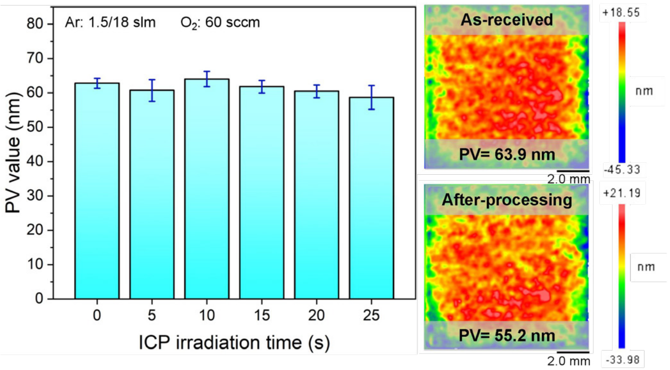

Fig. 4. The evolution of flatness during ICP irradiation.

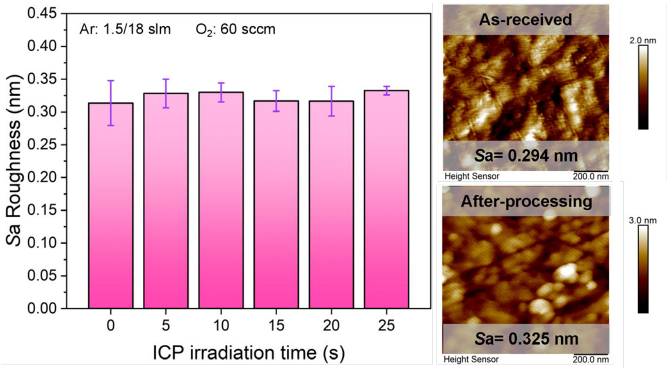

Fig. 5. The evolution of *S*a roughness during ICP irradiation.

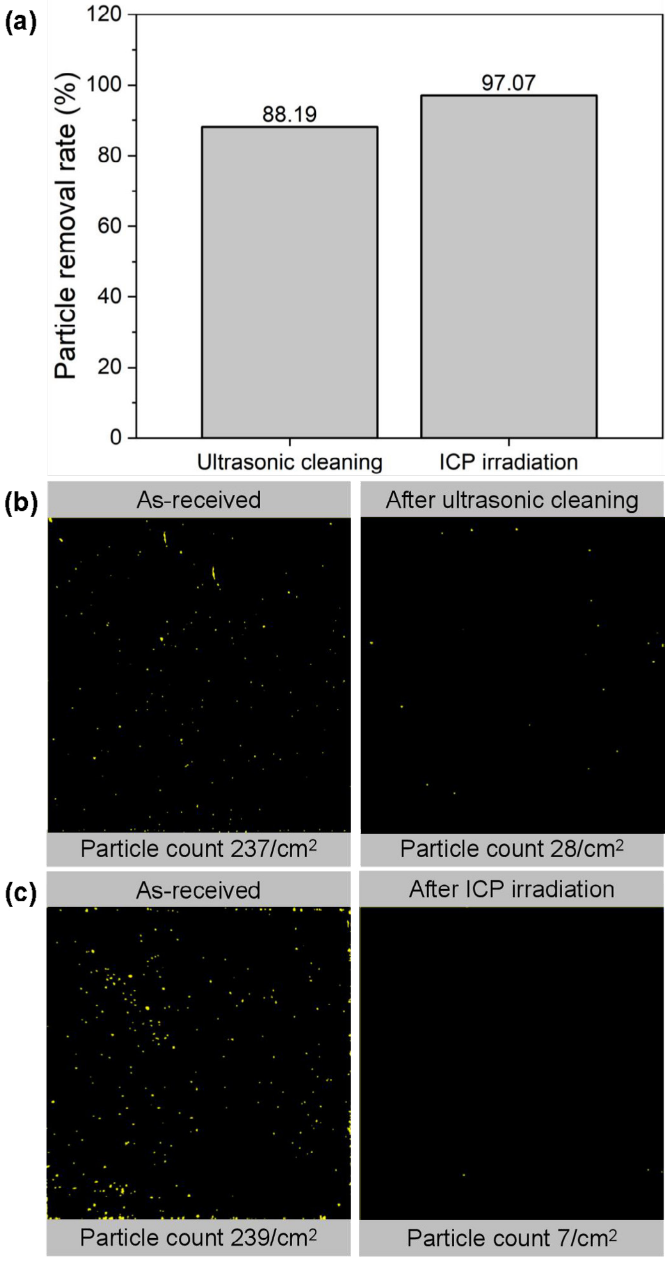

Fig. 6. (a) Particle removal rate after ultrasonic cleaning and after ICP irradiation; (b) Photographs of surface before and after ultrasonic cleaning; (c) Photographs of surface before and after ICP irradiation.

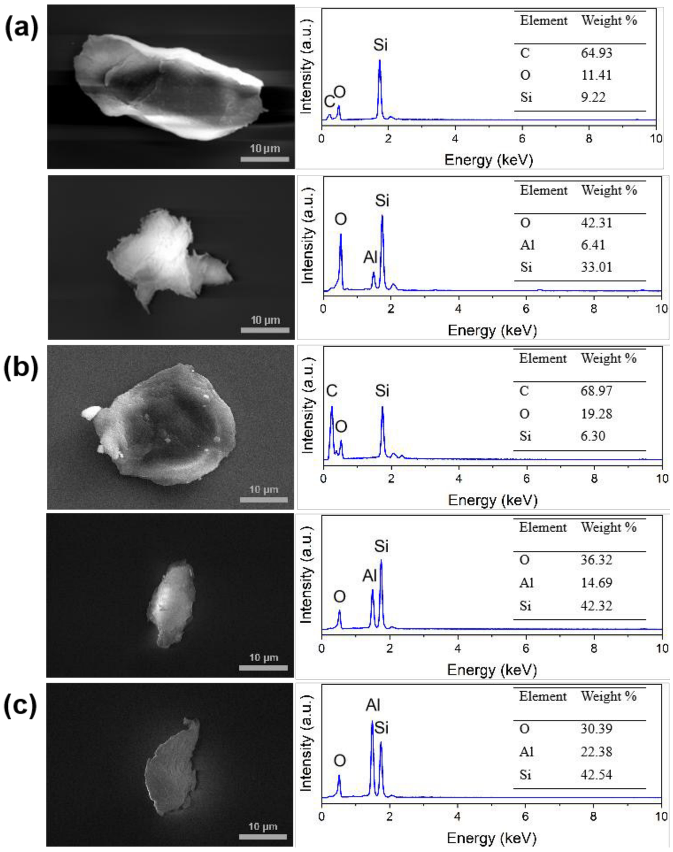

Fig. 7. (a) Residual contaminants of the original silica glass; (b) Residual contaminants after ultrasonic cleaning; (c) Residual contaminants after ICP irradiation.

Flatness is generally quantified with total thickness variation (TTV) or PV value. If the PV value is excessively large, it will lead to a large unbonded area, making direct bonding unfeasible [14]. The enormous thermal stress generated by the high temperature of the plasma is a potential threat to decreasing form accuracy. To mitigate this issue, we adopt a low RF power and the scanning mode to prevent excessive temperature buildup. Fig. 4 depicts the relationship between the PV value and the duration of ICP irradiation. The result demonstrates that the detrimental impact of high-temperature plasma on the surface flatness is mitigated by reducing RF power and employing scanning mode to dissipate heat during the entire treatment duration.

In order to accomplish direct bonding reliably by hydrogen bonding and van der Waals forces, it is crucial for the silica glass surface to be smooth (*S*a < 0.5 nm) [15]. As shown in Fig. 5, the surface roughness barely changed after ICP irradiation. Therefore, ICP irradiation maintained the flatness (PV < 70 nm) and roughness (*S*a < 0.4 nm) of the sample. The surface conditions after ICP irradiation met the requirements of direct bonding, thereby providing a high success rate for the direct bonding of silica glass.

3.3. Effect of ICP irradiation on surface cleaning

The quality of the direct bonding depends on the cleanliness of the surface. Surface contaminants from environmental or manufacturing process residues can cause the formation of voids at the bonding interface. The effects of ultrasonic cleaners and atmospheric ICP on the elimination of contaminants were compared.

The ImageJ software was employed to quantify the particle count on the surface of silica glass before and after ultrasonic cleaning for 3 min, as well as before and after ICP irradiation for 25 s. As shown in Fig. 6(a), after ICP irradiation, the particle removal rate reached 97.07%. In consequence, Fig. 6 clearly demonstrates that ICP is a more efficient and effective cleaning method compared to ultrasonic cleaning.

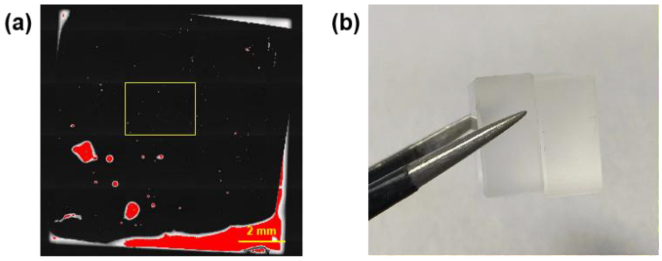

Fig. 8. (a) Image of the bonding interface by LSCM; (b) Photograph of glass-glass pre-bonded.pairs after ICP irradiation.

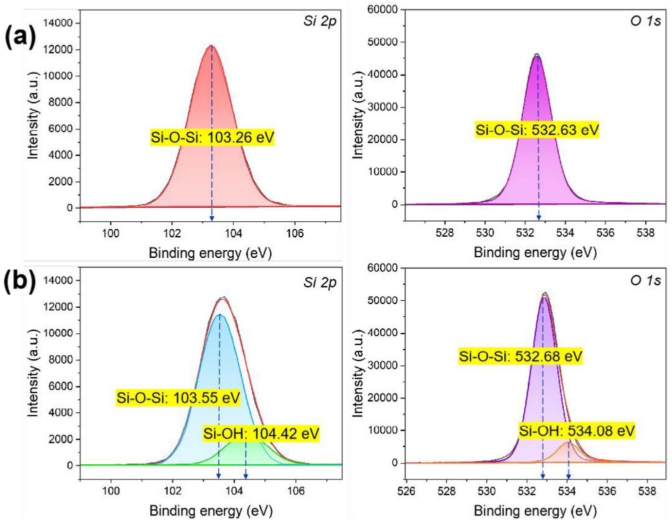

Fig. 9. *Si 2p* and *O 1s* XPS spectra of silica glass surfaces (a) Before ICP irradiation; (b) After ICP irradiation for 25 s.

The residual particle composition of the surface before and after ultrasonic cleaning and ICP irradiation was analyzed by SEM and EDS. As shown in Fig. 7(a), the presence of metal contaminants on the original surface of the silica glass can be attributed to the slurries used in CMP [16 - 18]. Additionally, the sample surface inevitably accumulates carbonaceous contaminants from the ambient air and manual operations. As presented in Fig. 7(b), the analysis revealed that residual particles consisting of elements such as metal, carbon, silicon and oxygen were present after ultrasonic cleaning. Due to the non-selective characteristic and limited ability of ultrasonic cleaning in particle removal, organic residues still remained on the surface. In contrast, Fig. 7(c) indicated that impurities containing carbon element are removed after ICP irradiation. The removal of carbonaceous contaminants might be attributed to the incorporation of oxygen into the plasma.

The silica glass, which has been activated by ICP, is pre-bonded, and the bonding interface is observed using LSCM. As shown in Fig. 8(a), the red area is the unbonded area and the black area is the bonded area. Unbonded areas were mainly concentrated at interface edges. This consequence can be the result of uneven pressure. The majority of the areas at the center of the bonding interface were pre-bonded, with only a few voids present because of residual particles. Fig. 8(b) shown the sample after pre-bonding.

3.4. Investigation of chemical effects

To investigate the effects of ICP irradiation on silica glass, the result of XPS is used to analyze changes in the chemical state of surfaces. The core-level spectra of *Si 2p* and *O 1s* for the silica glass before and after ICP irradiation were shown in Fig. 9 [19, 20]. After ICP irradiation, Si-OH peak were generated on the surface, and Si-O-Si peak were lower than the one before treatment. The results indicated that the high-energy Ar-O_2 plasma partially disrupted the intrinsic Si-O-Si bonds. Subsequently, these broken bonds recombined into silanol groups, which enhanced the surface's hydrophilicity.

4. Conclusion

In this work, we activated silica glass with high efficiency through ICP irradiation, resulting in the achievement of direct glass-glass bonding. The relationship between hydrophilicity of silica glass and ICP irradiation time was systematically studied. The results demonstrated that by employing ICP irradiation, the contact angle can be significantly reduced from 41.8° to less than 3° within mere 10 s. The surface undergoes a transformation into a superhydrophilic state in the atmospheric environment. What’s more, ICP irradiation maintained the original flatness (PV < 70 nm) and roughness (*S*a < 0.4 nm) of the sample. Ar-O_2 plasma was capable of effectively purging carbonaceous contaminants and other pollutants, thus facilitating the formation of a dense bonding interface. The result of XPS further explained that silanol groups can be created by high-energy plasma. To sum up, ICP irradiation is a promising activation method for the manufacturing of optical devices, which efficiently achieves direct bonding of silica glass without expensive vacuum equipment.

References

[1] Napoli M, Eijkel JC, Pennathur S. Nanofluidic technology for biomolecule applications: a critical review. Lab Chip; 2010.10(8):957-85.

[2] Xu Y, Jang K, Yamashita T, Tanaka Y, Mawatari K, Kitamori T. Microchip-based cellular biochemical systems for practical applications and fundamental research: from microfluidics to nanofluidics. Anal Bioanal Chem 402; 2012. p. 99-107.

[3] Xu Y, Wang C, Dong Y, Li L, Jang K, Mawatari K, Suga T, Kitamori T. Low-temperature direct bonding of glass nanofluidic chips using a two-step plasma surface activation process. Anal Bioanal Chem 402; 2012. p. 1011–1018.

[4] Granados L, Morena RM, Takamure N, Suga T, Huang S, McKenzie DR, Ho-Baillie AWY. Silicate glass-to-glass hermetic bonding for

encapsulation of next-generation optoelectronics: A review. Materials Today; 2021. p. 131-155.

[5] Arayanarakool R, Gac SL, Berg AVD. Low-temperature, simple and fast integration technique of microfluidic chips by using a UV-curable adhesive. Lab Chip; 2010.10:2115-2121.

[6] Haisma J, Spierings GACM. Contact bonding, including direct-bonding in a historical and recent context of materials science and technology, physics and chemistry: Historical review in a broader scope and comparative outlook. Materials Science and Engineering: R: Reports; 2002.37:1-60.

[7] Kalkowski G, Rothhardt C, Jobst PJ, Mark Schürmann, Ramona Eberhardt. Glass Direct Bonding for Optical Applications. ECS Transactions; 2013.

[8] Birckigt P, Grabowski K, Leibeling G, Flügel-Paul T, Heusinger M, Ouslimani H, Risse S. Effects of static load and residual stress on fused silica direct bonding interface properties. Applied Physics A; 2021.

[9] Funano SI, Ota N, Tanaka Y. A simple and reversible glass–glass bonding method to construct a microfluidic device and its application for cell recovery. Lab on a Chip; 2021.

[10] Zhou J, Mei N, Leonenko Z, Zhou N, Mayer M. Direct glass-to-glass bonding obtained via simplified ammonia-based low-temperature procedure resists high shear stress and powerful CW fiber laser irradiation. RSC Adv.; 2022.12(48):31016-31023.

[11] Shirai K, Mawatari K, Kitamori T. Extended nanofluidic immunochemical reaction with femtoliter sample volumes. Small; 2014.10(8):1514-22.

[12] Fang Z, Zhang Y, Li R, Liang Y, Deng H. An efficient approach for atomic-scale polishing of single-crystal silicon via plasma-based atom-selective etching. International Journal of Machine Tools and Manufacture; 2020.

[13] Fournel F, Martin-Cocher C, Radisson D, Larrey V, Beche E, Morales C, Delean PA, Rieutord F, Moriceau H. Water Stress Corrosion in Bonded Structures. ECS J. Solid State Sci. Technol.; 2015. p. 124.

[14] Bao S, Wang Y, Lina K, Zhang L, Wang B, Sasangka WA, Lee KEK, Chua SJ, Michel J, Fitzgerald E, Tan CS, Lee KH. A review of silicon-based wafer bonding processes, an approach to realize the monolithic integration of Si-CMOS and III–V-on-Si wafers. J. Semicond.; 2021.

[15] Plößl A, Kräuter G. Wafer direct bonding: tailoring adhesion between brittle materials. Materials Science and Engineering: R: Reports; 1999.25:1-88.

[16] Mahadevaiyer K, Jakub WN, Lee MC. Chemical mechanical planarization: slurry chemistry, materials, and mechanisms. Chem Rev.; 2010.110(1):178-204.

[17] Lefevre, Paul. Defects Observed on the Wafer after the CMP Process. Microelectronic Applications of Chemical Mechanical Planarization; 2007. p. 511-561.

[18] Tseng, W.-T. Approaches to defect characterization, mitigation, and reduction. In Advances in Chemical Mechanical Planarization (CMP); 2016. p. 433-462.

[19] Wang C, Qi X, Wang Y, Wu B, Tian Y. Room-Temperature Direct Heterogeneous Bonding of Glass and Polystyrene Substrates. Journal of The Electrochemical Society; 2018. 165.

[20] Zhang Y, Zhu L, Chen L, Wu B, Liu L, Ye G. Influence of Magnesia on Demoulding Strength of Colloidal Silica-Bonded Castables. REVIEWS ON ADVANCED MATERIALS SCIENCE; 2019. p. 32-57.