Hybrid plasma bonding of germanium and glass wafers at low temperature

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Hybrid plasma bonding (i.e., sequentially plasma activation followed by anodic bonding) has been demonstrated for germanium and glass wafers for the first time. Void-free interface with high bonding strength has been observed at 200 °C. This improved quality is attributed to reduced surface roughness and increased hydrophilicity of sequentially activated germanium and glass. Three layers caused by reactions of OH molecules between the highly reactive surfaces after plasma activation and opposite migration of cations and anions are observed across the interface.

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1. Introduction

Germanium (Ge) has recently drawn considerable interest for the fabrication of photodetectors for long distance optical communication systems operating in 1300–1550 nm wavelength range. This is because of large absorption coefficient of Ge at near infrared frequency range [1]. Furthermore, being a group-IV material, Ge is compatible with silicon (Si) technology and offers high carrier mobility. Therefore, Ge on Si (GOS) technology is competing with III–V on Si technology [2]. The GOS technology has been implemented for photodetector fabrication by epitaxial growth of Ge on Si at temperatures in the range of 700–900 °C [3]. However, epitaxial growth of Ge is not preferable because of the incompatibility of high temperature with microelectronics. Also, this process is expensive and creates high concentration of misfit and threading dislocations in the deposited Ge film due to large lattice mismatch (4.2%) between Ge and Si. The dislocations create large dark current and reduce the detector sensitivity [4]. In contrast, direct wafer bonding (DWB) and layer splitting process allow thin film of Ge with bulk properties on a variety of substrates. The DWB, being a low cost, high throughput process, has found a wide range of applications [5]. Recently, Ge on Si photodetector has been realized using wafer bonding and smart-cut process [6,7].

On the other hand, glass is a low cost material with good optical transparency and dielectric property in a wide range of frequency, high chemical and heat resistivity, and high mechanical strength [8]. Direct bonding of Ge and glass can be used in fiber optic receivers, where Ge photodetector bonds with fiber end. Recently, Ge-on-glass photodetector has been realized using DWB [2,9]. However, high temperature (~400 °C), chemical, and long time annealing (~8 h) were needed. In fact, high

bonding temperature creates thermal stress, interfacial voids and hence not preferable for delicate structures and materials with large difference in thermal expansion coefficient [10]. Chemical sensitivity of Ge hinders the applicability of these bonding techniques [11]. Furthermore, long time annealing reduces device throughput. Hence, a low temperature, chemical free, void-free robust bonding, and fast technique for improved bonding quality of Ge and glass is needed for practical applications. For example, high bonding strength at low temperature is essential in Ge layer transfer to glass through back end thinning process. While Ge bonding with silicon and glass has been implemented in the fabrication of optical devices [2,6,7,9] and it has tremendous need in emerging applications such as optical biosensing system [12], low temperature bonding mechanism of Ge and glass has not been yet investigated.

This article reports a chemical free, strong and fast hybrid plasma bonding (HPB) of Ge and glass at 200 °C. The HPB process consists of three steps: (1) surface activation by oxygen (O$_2$) reactive ion etching (RIE) plasma followed by (2) surface activation by nitrogen (N$_2$) microwave (MW) radicals and (3) then anodic bonding in air. The bonding method that combines the surface activation mentioned in the first two steps is known as sequentially plasma activated bonding (SPAB). The bonding quality has been explored using tensile pulling test. To understand the bonding mechanism, high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis (EDX), contact angle and surface roughness measurements have been performed.

2. Experimental

Commercially available CZ-grown one-side polished 2-in. 525 ± 25 µm thick, n-type (100) Ge wafers and double side polished Pyrex 7740 borosilicate 4-in. 500 ± 25 µm thick glass wafers have been used. The major elements in the Pyrex glass are SiO$_2$ (80.93%) including B$_2$O$_3$

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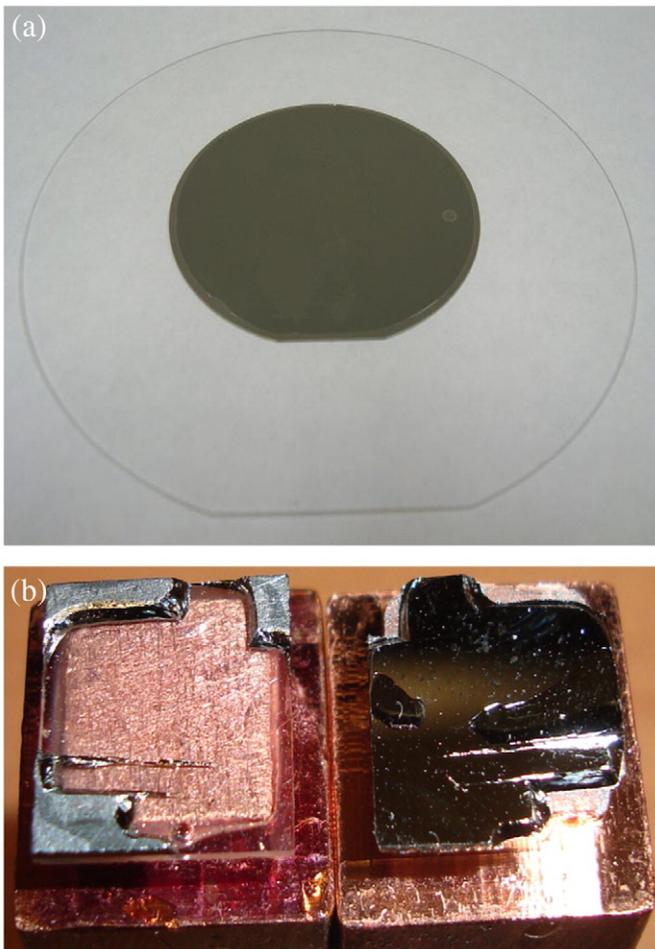
Fig. 1. (a) Optical images of hybrid plasma bonded Ge/glass. (b) Fracture images of bonded Ge/glass after tensile pulling test.

(12.7%), Na_2O (4.00%), Al_2O_3 (2.30%), K_2O (0.04%) and Fe_2O_3 (0.03%). A wafer level HPB system has been used for the bonding. Details of the HPB system can be found elsewhere [13]. The surfaces of Ge and glass were first activated using a 50 W O_2 RIE plasma for 15 s at 60 Pa followed by activation using a 2500 W N_2 MW radical for 30 s at 60 Pa. Then the wafers were contacted in clean room ambient and finally cold-rolled under 0.2 MPa. The contacted wafers were further treated with anodic bonding at 200 °C and 1 kV for 10 min. The plasma parameters have been chosen based on our previous study [14].

3. Results and discussion

Fig. 1a shows the optical image of the hybrid plasma bonded Ge/glass wafers. Although voids were observed at the interface in the SPAB before the anodic treatment, a nearly void-free interface was achieved in the HPB. This is attributed to absorption of voids in the interfacial oxide [13]. The voids remained were presumably due to the presence of particle on the activated surface and entrapment of air at the interface due to plasma induced surface defects [14].

Table 1
Contact angle of DI water on Ge and glass surfaces.

Specimen	Contact angle [°]		
	Before plasma activation	After RIE plasma activation	After sequential plasma activation
Ge	68	<2	<2
Glass	29	25.3	17.7

The bonding strength of Ge/glass interface was investigated by tensile pulling test. The bonding strength was 9.1 MPa. Fig. 1b shows the fracture image of bonded Ge/glass interface after tensile pulling test. The images show a partial fracture in the bulk of Ge. It also shows that the fractured Ge was remained on glass wafer after the bonding test. The bulk fracture of Ge is due to the high bonding strength of the bonded interface. The high bonding strength (robust) is very important in layer transfer process. In layer transfer process, either the bulk or the exfoliated surfaces (which are rough) from the bonded wafers need to be thin down or smoothening by chemical mechanical polishing (CMP). This CMP process requires strong bonding strength of the interface. It has been reported that after surface smoothening process the performance of photo detector significantly improved [9].

To explore the bonding mechanism of Ge and glass, contact angle measurements were performed after each step of plasma activation. Table 1 shows the contact angle of a drop of deionized water droplet (10 µL) on Ge and glass surface before plasma activation, after the RIE plasma activation and after the sequential plasma activation. Before activation the water contact angle on Ge surface was 68° and it was below the detection limit of the instrument after the RIE and the sequential plasma activation. This result is consistent with recently reported results on Ge surface hydrophilicity [15]. On the other hand, the contact angle on glass surface was 29, 25.3 and 17.7° before activation, after the RIE plasma activation and after the sequential plasma activation respectively. The decrease in contact angle refers to increase in surface hydrophilicity. Surface hydrophilicity is a measure of surface energy and the bonding strength. From the Young's equation in equilibrium [15], the higher the hydrophilicity (the lower the contact angle), the higher the surface energy. This has experimentally been proved and reported in [16]. This implies that the high bonding strength of Ge/glass interface in hybrid plasma bonding is due to the increase in surface energy. Before activation, the wafer surfaces are usually covered with native oxides, contaminations, and particles. In general, the RIE plasma activation removes contaminations, particles and forms a porous oxide layer by physical sputtering process [14]. Since the RIE power was low (i.e., 50 W), the surface was terminated by a large number of dangling bonds (free bond) on the partially remained native oxides at the surface. In clean room ambient, these dangling bonds are covered with a large number of –OH groups. This surface is easy to wet with the deionized water and hence the contact angle reduced after RIE plasma activation.
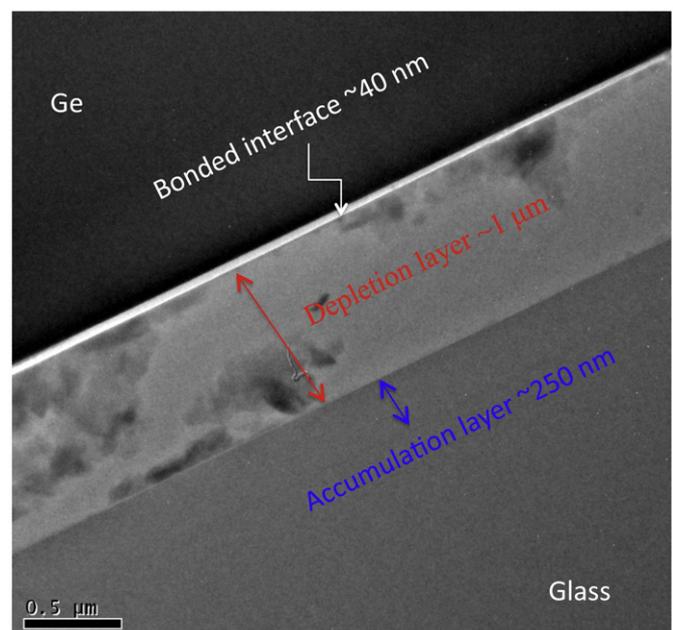
Fig. 2. HRTEM images of hybrid plasma bonded Ge/glass interface.

Further reduction in the contact angle was observed after the sequential plasma activation due to reactivity of MW radicals [17].

Fig. 2 shows a HRTEM image of bonded Ge/glass interface. A ~1 μm thick brighter layer than Ge and glass was observed in glass near the bonded interface. This layer looks similar to a depletion layer at the interface of Si and Pyrex glass observed in anodic bonding [18] and hybrid bonding [13]. The observed depletion layer in glass was due to the migration of alkaline cations from the region near the interface toward the bulk. For identical plasma activation parameters, we observed a ~353 nm depletion layer in hybrid bonded Si/glass, as reported in [13]. In addition to the depletion layer, a ~250 nm thick second layer in glass was observed near the Ge/glass interface. This is due to accumulation of alkaline cations [19]. Furthermore, a thin layer (~40 nm) relatively with higher contrast than that of the depletion layer was observed at the bonded interface. This brighter layer is thicker than that of the Si/Si interface in the SPAB [17]. The interfacial Si/Si layer in the SPAB has been identified as Si suboxide [20]. Similarly, Ge oxide can be formed at the Ge/glass interface in the SPAB. Further enlargement of the Ge oxide can be attributed to the anodic bonding after the SPAB (i.e., HPB). Therefore, the increased thickness of the brighter layer is due to the growth of Ge oxide caused by the opposite migration of oxygen anions to that of the alkaline cations.

To investigate the elemental distribution at the interface, energy dispersive X-ray (EDX) analysis was performed. Fig. 3 shows the distribution of Ge and three main elements of Pyrex glass at and around the interface. From Fig. 3(a), it is evident that Ge did not diffuse into glass. From Fig. 3(b) and (c), the presence of oxygen and Si was evident in the depletion layer. A considerable amount of oxygen was observed across the interface, which enlarged the thickness of Ge oxide. Diffusion

of oxygen in Ge was not found at the interface. Fig. 3(d) shows the presence of sodium (Na) in Ge, the reason for this is not clear from this study. Na and B were not observed in the depletion region. In fact, EDX does not detect boron [21]. Therefore the HRTEM results could not fully be explained using the EDX study. Further study is planned.

The characteristic behavior of surface controls the bonding performance. For practical applications such as optical biosensing system [22], the surface roughness of glass needs to be kept as low as possible in order to achieve high reflectivity of the surface [23]. Fig. 4 shows the atomic force microscopy (AFM) (ICON from Veeco) images of Ge and glass before plasma activation, after RIE plasma activation and after sequential plasma activation. The scanning was done in tapping mode over an area of $2 \times 2\,\mu m^2$. Table 2 summarizes the root mean square (RMS) surface roughness of Ge and glass. The surface roughness of glass was relatively higher than that of Ge. This was due to the sensitivity discrepancy between the alkaline and silicate elements of glass to CMP. This results in nanodefects on glass surface in contrast to Si [24]. These nanodefects cause voids at the bonded interface, as shown in Fig. 1a. In fact, the surface roughness of the sequential plasma activated Ge and glass was remarkably reduced. The decrease in surface roughness improved the surface energy and the bonding strength [15,20]. This reduction is attributed to removing surface contaminations, and native oxides. The improved surface roughness indicates that the hybrid plasma bonding of Ge/glass can be used for the level-free detection of biological species using optical biosensing system.

4. Conclusions

Hybrid plasma bonding (HPB) has been demonstrated for Ge/glass bonding to achieve a void-free robust bonding at 200 °C under an
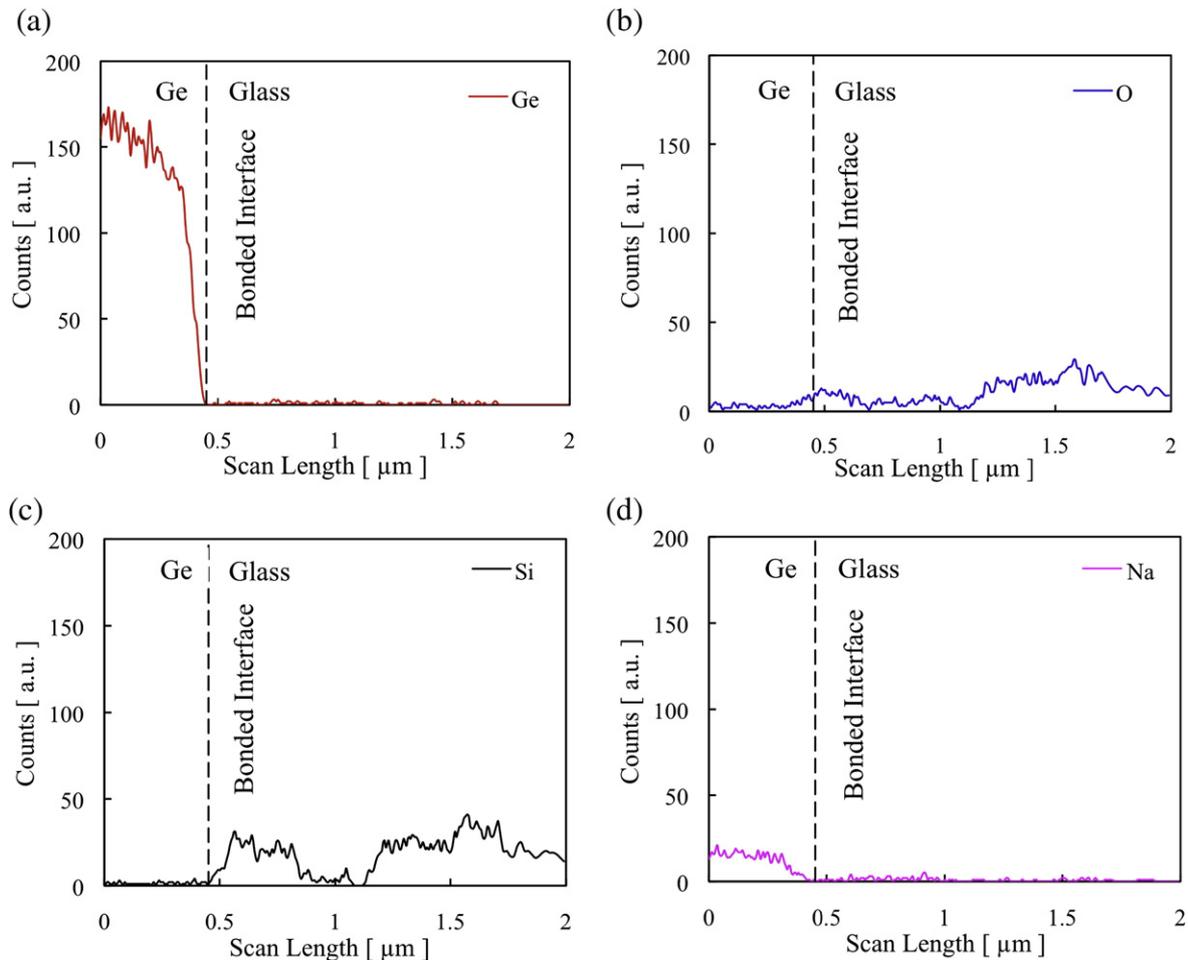
Fig. 3. EDX spectra of (a) Ge, (b) O, (c) Si and (d) Na at and around the interface of hybrid plasma bonded Ge/glass.
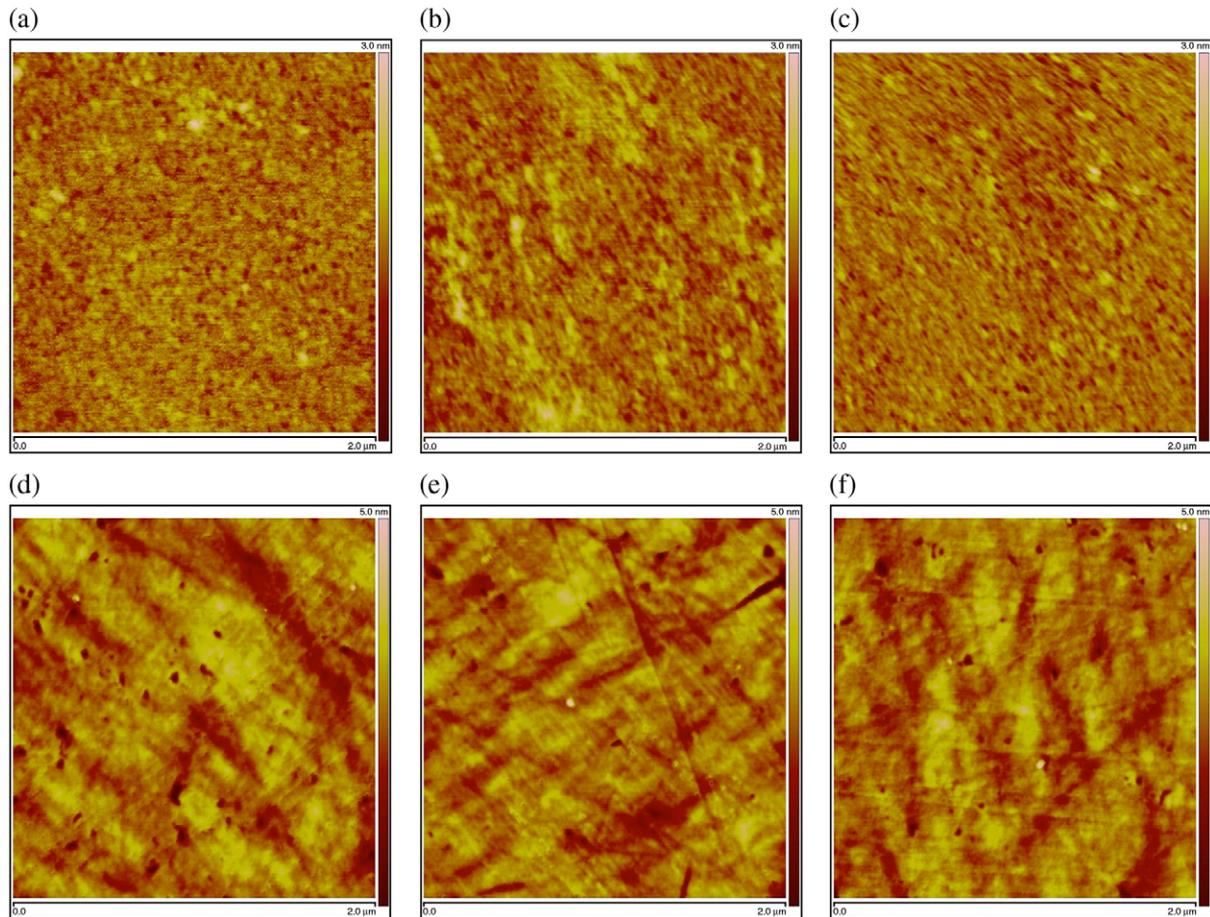
Fig. 4. AFM images of Ge (a) before plasma activation (b) after RIE plasma activation (c) after sequential plasma activation and AFM images of glass (d) before plasma activation (e) after RIE plasma activation (f) after sequential plasma activation.

applied field of 1 kV. The bonding strength was 9.1 MPa. The high bonding strength was due to cleanliness and high reactivity of surface after the sequential plasma activation. The SPAB followed by anodic treatment (i.e., HPB) resulted in three layers: a 1 micrometer thick depletion, a 250 nm thick alkaline and a ~40 nm thick Ge oxide layers across the interface. The bonding mechanism of Ge/glass is attributed to the reactions of OH molecules between the highly reactive surfaces in the SPAB, and the opposite migration of cations and anions during anodic treatment. This method can be used in optical biosensing system for level-free detection of biological species due to improved surface roughness of glass and robust interface of Ge/glass.

Acknowledgements

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Table 2
RMS surface roughness of Ge and glass.

Specimen	RMS surface roughness [nm]		
	Before plasma activation	After RIE plasma activation	After sequential plasma activation
Ge	0.24	0.25	0.20
Glass	0.52	0.48	0.46