Interfacial Reactions between Si and SiO$_2$ with Ceramic Additives

Yu-Hsiang Chen 1*, Kun-Lin Lin 2* and Chien-Cheng Lin 1

Abstract: In this study, 10 wt.% ceramics—Al$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$, MgO, and TiO$_2$—were employed as additives for amorphous SiO$_2$ after pressing and annealing at 1300 °C. The amorphous SiO$_2$ changed to cristobalite SiO$_2$. Through X-ray diffraction, scanning electron microscopy, and transmission electron microscopy with energy-dispersive spectrometry, the reaction phases of La$_2$Si$_2$O$_7$, Y$_2$Si$_2$O$_7$, and MgSiO$_3$ (Mg$_2$SiO$_4$) were found in the SiO$_2$ with 10 wt.% La$_2$O$_3$, Y$_2$O$_3$, and MgO additives. Cracks formed in the Si and SiO$_2$–ceramic additive sites because of the difference in the coefficients of thermal expansion among the Si, SiO$_2$, ceramic additives, and reaction phases. After Si came into contact with the SiO$_2$–ceramics, two types of microstructures were found: those with and those without an amorphous SiO$_2$ reaction layer at the interface. Amorphous SiO$_2$ layer formation is due to the replacement of the Si position in SiO$_2$ by Al$^{3+}$ and Ti$^{4+}$ impurities, which can break the bonds between Si atoms. The O content in the Si decreased from $6–9 \times 10^{17}$ atoms/cm$^3$ for SiO$_2$ to less than $1 \times 10^{16}$ for SiO$_2$–Al$_2$O$_3$ and SiO$_2$–MgO. The average resistivity of the Si was 3 Ω·cm for SiO$_2$ and decreased to 0.12–0.36 Ω·cm for the SiO$_2$ with ceramic additives.

Keywords: ceramic crucible; silicon; interface; Si joint; crystal growth

1. Introduction

Modern integrated circuits and electronic devices are mainly manufactured using single-crystal Si wafers produced using the Czochralski (CZ) pulling technique. The CZ method is based on crystal pulling from Si melt, for which a quartz crucible is placed in the hot zone to melt polysilicon. The quartz crucible is softened at high temperatures during the thermal pulling process; thus, the crucible must be secured by a graphite crucible to prevent deformation. Many types of defects are generated in Si ingots after thermal pulling, such as vacancies, interstitial defects, oxidation-induced stacking faults, and pits, because O from the quartz crucible diffuses into the Si ingot [1–7].

Quartz is a mineral comprising Si and O atoms in a continuous SiO$_4$ tetrahedral framework, with each O atom shared between two tetrahedra, resulting in the overall chemical formula of SiO$_2$. Si inclusions and worm-like cristobalite SiO$_2$ appear locally at the Si–SiO$_2$ interface because of the solution–precipitation mechanism, as was demonstrated through scanning electron microscopy (SEM) [8]. Local cristobalite SiO$_2$ can result in crack formation on the Si surface. When the Ba concentration in silica glass is $>30$ ppm, cristobalite SiO$_2$ changes to a dense, smooth, continuous layer and results in decreased precipitation of Si inclusions and defects [9,10]. The Ba-doped cristobalite layer is formed through heterogeneous nucleation caused by Ba additives. In addition to Ba additives [9,10], high-purity silica [11], Si$_3$N$_4$ [12–14], and SiC [15] coatings on a crucible can considerably affect the lifetime of Si ingots. A high-purity silica and SiC coating on a crucible can act as a diffusion barrier layer and improve ingot quality [11,15]. Most crucibles used for single-crystal Si growth are made from SiO$_2$ (quartz), but alternative ceramic materials for use in Si crystal growth have gained research attention. Lin et al. [16] studied three types of ceramic plates—Al$_2$O$_3$, ZrO$_2$, and quartz (SiO$_2$)—for contact with a Si wafer.
through annealing at 1450 °C, and they noted that defects appeared at the Si–ceramic interface. Using SEM and transmission electron microscopy (TEM), they found a crack and a dislocation pile-up at the Si–SiO₂ interface; two intermetallic compounds, Y₂Si₂O₇ and ZrSis₂, at the Si–ZrO₂ interface; and no intermetallic compounds and few defects at the Si–Al₂O₃ interface. Furthermore, the oxygen concentration and electrical resistivity near the interface were high, and they gradually decreased as the distance from the Si–ceramic interface increased [16]. Therefore, the ceramics in contact with Si could result in defect formation, oxygen aggregation, and/or the reaction barrier layers on the surface of Si. It is significant to clarify which types of ceramics affect the defects, oxygen diffusion, and resistivity change at the Si interface after being in contact with Si. The purpose of the present study is to choose different valence electrons of ceramics, such as Mg⁺²⁺, Al⁺³⁺, La⁺³⁺, Y⁺³⁺, and Ti⁺⁴⁺, to place in contact with Si and then evaluate the electrical property of Si due to the charge balance effect and the formation of defects and effective barrier layers on the Si–ceramics. In the present study, 10 wt% ceramics—Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂—were separately added to amorphous SiO₂ after pressing and annealing at 1300 °C for single-crystal Si growth. The microstructures of the Si/SiO₂–additive interfaces were characterized using SEM and TEM in conjunction with energy-dispersive spectroscopy (EDS). In addition, the concentration of O and the resistivity of the Si after contact with the ceramics were measured and are discussed herein.

2. Experimental Procedures

Al₂O₃ (aluminum oxide powder, Sigma-Aldrich, St. Louis, MO, USA, ≤10 µm, 99.5%), La₂O₃ (lanthanum oxide, Cerac, Inc., Milwaukee, WI, USA 325 mesh, 99.9%), Y₂O₃ (yttrium oxide, Sigma-Aldrich, St. Louis, MO, USA, 99.999%), MgO (magnesium oxide nano powder, Inframat Advanced Materials, Manchester, CT, USA, 30-nm, 99.9%), and TiO₂ (titanium oxide, NOAH Technologies, San Antonio, TX, USA, 325 mesh, 99.9%) powders (10 wt %) were separately added to amorphous SiO₂ after pressing and annealing at 1300 °C for single-crystal Si growth. The microstructures of the Si/SiO₂–additive interfaces were characterized using SEM and TEM in conjunction with energy-dispersive spectroscopy (EDS). In addition, the concentration of O and the resistivity of the Si after contact with the ceramics were measured and are discussed herein.
were performed based on the principle of the Cliff–Lorimer [17] standard-less method. TEM specimens of Si–ceramic joints were prepared by conventional mechanical polishing and focused ion beam (FIB, FEI NovaLab 600). The quantitative composition analyses were performed based on the principle of the Cliff–Lorimer [17] standard-less method. Additionally, in order to accurately calculate the lattice parameters of reaction products, the image magnification of TEM was calibrated using the MAG*I*CAL reference standard sample (Norrox Scientific Ltd., Beaver Pond, ON, Canada). The pieces of Si from Si–ceramic joints were cut along a direction longitudinal to the interface for the residual oxygen and resistivity measurements. The concentration evaluation of the residual oxygen in Si by Fourier-transform infrared spectroscopy (FTIR, Bruker VERTEX 70) was performed based on the ASTM F 1188 method [18], and the resistivity of Si was measured by four-point probe resistance meter (RT-80, Napson Corporation, Tokyo, Japan).

\[ L_s = \left( \frac{d_0 - d}{d_0} \right) \times 100\% \]

<table>
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<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>10wt% Al₂O₃</th>
<th>10wt% La₂O₃</th>
<th>10wt% Y₂O₃</th>
<th>10wt% MgO</th>
<th>10wt% TiO₂</th>
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<td>After 1300°C 2hr</td>
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<td>24.97%</td>
<td>26.66%</td>
<td>27.77%</td>
<td>24.52%</td>
<td>27.40%</td>
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<td>Linear shrinkage</td>
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![Figure 1](image1.png)  
Figure 1. Photograph of green bodies and sintered (1300 °C for 2 h) samples of SiO₂ and SiO₂ with ceramic additives.

![Figure 2](image2.png)  
Figure 2. Schematic of (a) graphite crucible and (b) Si and SiO₂–ceramic additive interface. (c) Cross-sectional photograph of Si contact with SiO₂–TiO₂. (d) Diagram of several pieces of Si cut longitudinally with respect to the interface after contact for evaluation of O concentration and electrical resistivity.

3. Results and Discussion

Figure 3 shows the XRD spectra of the pure SiO₂ and the SiO₂ with 10 wt.% Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂. Before sintering, the crystal structure of the SiO₂ tended
to be in the amorphous phase (broad peak at ~20°) and then changed to a combination of the amorphous phase and cristobalite tetragonal phase (reference code: 01-076-0940, crystal system: tetragonal, space group: P41212(92), 𝛼 = 𝛽 = 𝜎 = 90°) after sintering at 1300 °C, as indicated by the sharp peak at ~20° in Figure 3a. The Al₂O₃ and TiO₂ additives did not react with the SiO₂ to form other phases (Figure 3b,f). The other ceramic additives, La₂O₃, Y₂O₃, and MgO, reacted with the SiO₂ to form other reaction phases in the samples. For example, La₂Si₂O₇, Y₂Si₂O₇, and MgSiO₃ (Mg₂SiO₄) phases were found with the addition of 10 wt.% La₂O₃ (Figure 3c), Y₂O₃ (Figure 3d), and MgO (Figure 3e), respectively. The corresponding chemical formulas are 2SiO₂ + La₂O₃ = La₂Si₂O₇, 2SiO₂ + Y₂O₃ = Y₂Si₂O₇, and SiO₂ + MgO = MgSiO₃ or SiO₂ + 2MgO = Mg₂SiO₄.

Figure 3. XRD spectra of (a) SiO₂ and (b–f) SiO₂ with 10 wt.% Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂, respectively.

Figure 4 shows the SEM and backscattered electron images (BEIs) for the SiO₂ and the SiO₂ with 10 wt.% Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂ additives, showing that no other reaction phase was formed after the addition of Al₂O₃ (Figure 4b) or TiO₂ (Figure 4f). However, the reaction phases La₂Si₂O₇, Y₂Si₂O₇, and MgSiO₃ were found with the La₂O₃ (Figure 4c), Y₂O₃ (Figure 4d), and MgO (Figure 4e) additives. The reaction phases were further confirmed using TEM. Figure 5 shows the TEM bright-field images (BFIs) and the selected area diffraction patterns (SADPs) of the Si with 10 wt.% Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂ additives after sintering at 1300 °C in Ar. Through SADP indexing and EDS and TEM, the composition of Al₂O₃, La₂Si₂O₇, Y₂Si₂O₇, MgSiO₃, and TiO₂ (Figure 6f) and the reaction phases (La₂Si₂O₇, Y₂Si₂O₇, and MgSiO₃) in the SiO₂ with ceramic additives were identified.

Through XRD (Figure 3), SEM (Figure 4), and TEM (Figure 5), the microstructures and reaction phases were thoroughly examined in the sintered SiO₂–ceramic additives. After the reaction between the Si and the sintered SiO₂–ceramic additives, two types of microstructures were identified: those with and those without a reaction layer at the interface. Figure 6 shows the BEIs/SEM images for the Si/SiO₂ and Si/SiO₂–La₂O₃, Si/SiO₂–Y₂O₃, and Si/SiO₂–MgO interfaces, showing the absence of a reaction layer. Cracks formed in the Si and SiO₂–ceramics because of a coefficient of thermal expansion (CTE) mismatch. XRD (Figure 3) revealed amorphous SiO₂ (broad peak) and cristobalite SiO₂ in the SiO₂ and SiO₂–ceramics. The difference in the CTEs of amorphous SiO₂ (0.5 × 10⁻⁶/K) [19] and cristobalite SiO₂ (14.5 × 10⁻⁶/K) [20] is large and, thus, resulted in
Figure 4. BEIs/SEM images of (a) SiO$_2$ and (b–f) SiO$_2$ with 10 wt.% Al$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$, MgO, and TiO$_2$, respectively.

cracks in the SiO$_2$ (Figure 6a). In Figure 6b–d, cracks are observable in the SiO$_2$–ceramics (with 10 wt.% La$_2$O$_3$, Y$_2$O$_3$, and MgO) because of the CTE mismatch between the SiO$_2$ and the reaction phases La$_2$Si$_2$O$_7$ (6 × 10$^{-6}$/K) [21], Y$_2$Si$_2$O$_7$ (3.9 × 10$^{-6}$/K) [22], and MgSiO$_3$ (47.7 × 10$^{-6}$/K) [23]. The CTEs of cristobalite SiO$_2$, La$_2$Si$_2$O$_7$, Y$_2$Si$_2$O$_7$, and MgSiO$_3$ are larger than those of Si (2.6 × 10$^{-6}$/K) [24]. Therefore, the Si endured compressive stress at the SiO$_2$ site, resulting in cracks near the interface. Furthermore, the CTE of MgSiO$_3$ is high (~47.7 × 10$^{-6}$/K) and, therefore, resulted in severe cracks in the Si near the interface (Figure 6d).

O in Si severely hinders Si ingot growth [3,4]. To evaluate the O content in the Si near and far from the Si–SiO$_2$ interface, EDS line scanning of TEM was performed. Figure 7 shows the BFIs/TEM images and EDS line scans of the Si–SiO$_2$, Si–SiO$_2$–La$_2$O$_3$, Si–SiO$_2$–Y$_2$O$_3$, and Si–SiO$_2$–MgO interfaces, showing the elemental distribution at the SiO$_2$ and Si sites. The O content was approximately 10 at.% in the Si near the interface for the SiO$_2$ with no ceramic additives (Figure 7a). When ceramics were added, the O content in the Si near the interface decreased to approximately 3 at.% for the La$_2$O$_3$ additive (Figure 7b) and approximately 8 at.% for the Y$_2$O$_3$ and MgO additives (Figure 7c,d).
Figure 5. (a–e) BFIs/TEM images and inserted SADP of Si–10 wt.% Al$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$, MgO, and TiO$_2$ interfaces after sintering at 1300 °C in Ar, respectively. (f) EDS summary of reaction phases (La$_2$Si$_2$O$_7$, Y$_2$Si$_2$O$_7$, and MgSiO$_3$) and ceramic additives (Al$_2$O$_3$ and TiO$_2$) in SiO$_2$.

Figure 6. BEIs/SEM images of (a) Si/SiO$_2$, (b) Si/SiO$_2$–10 wt.% La$_2$O$_3$, (c) Si/SiO$_2$–10 wt.% Y$_2$O$_3$, and (d) Si/SiO$_2$–10 wt.% MgO interfaces.
A reaction layer formed at the interface of the Si with SiO$_2$–Al$_2$O$_3$ and SiO$_2$–TiO$_2$, as shown in the BEIs/SEM images in Figure 8. TEM was used to analyze the reaction layer at the interface (Figure 9). Figure 9a,b show the BFIs/TEM images, EDS line scans, and SADPs for the Si/SiO$_2$–Al$_2$O$_3$ and Si/SiO$_2$–TiO$_2$ interfaces, respectively. No diffraction spots were found in the SADP of the reaction layer or the cristobalite SiO$_2$, as shown by the spot patterns (white arrows) in the SADP shown in Figure 9a,b. The reaction layer mainly comprised Si and O, as well as small quantities of Al (~8 at.%) and Ti (~2 at.%), as shown in the EDS images in Figure 9a,b, respectively. From the SADP and EDS results, the reaction layer could be identified as amorphous SiO$_2$ with small quantities of dissolved Al or Ti. Furthermore, the amorphous SiO$_2$ reaction layer effectively restricted O diffusion into the Si, as indicated by the O content of approximately 2 at.% and <0.8 at.% in the EDS line scans in Figure 9a,b, respectively. The mechanism underlying the formation of the amorphous SiO$_2$ reaction layer is shown in Figure 10. Figure 10a shows a schematic of crystalline SiO$_2$, revealing the tetrahedral arrangement of one Si atom bonded to four O atoms; in the image, most O atoms are bridged to two Si atoms, and two tetrahedra are joined at a corner to form the regular crystal structure of quartz. When the SiO$_2$–Al$_2$O$_3$ and SiO$_2$–TiO$_2$ came into contact with the Si substrate, the Si, O, Al, and Ti atoms diffused toward the Si site. The O from the SiO$_2$ site easily diffused into the Si substrate; this finding is supported by the diffusivity of the Al ($1.073 \times 10^{-11}$ cm$^2$/s) [25], Ti ($1.162 \times 10^{-8}$ cm$^2$/s) [26], and Si ($1.073 \times 10^{-11}$ cm$^2$/s) [25].
Si (8.610 × 10^{-14} \text{ cm}^2/\text{s}) [27], and O (1.429 × 10^{-10} \text{ cm}^2/\text{s}) [28] in the Si at 1200 °C. The results indicate that Al atoms could remain at the SiO₂ site because of their lower diffusivity than that of the O near the interface. Another possible explanation is the formation of native oxynitride on the Si surface, which blocks Al and Ti diffusion into the Si [29]. Thus, numerous Al and Ti atoms aggregated at the SiO₂ near the interface and resulted in the formation of amorphous SiO₂ because of the replacement of the Si position in the SiO₂ with Al^{3+} and Ti^{4+} impurities, which can break the bonds between Si and O, as shown in Figure 10b [30].

Figure 8. BEIs/SEM images of (a) Si/SiO₂–10 wt.% Al₂O₃ and (b) Si/SiO₂–10 wt.% TiO₂ interfaces.

Figure 9. BFIs/TEM images, EDS line scans, and SADPs of (a) Si/SiO₂–10 wt.% Al₂O₃ and (b) Si/SiO₂–10 wt.% TiO₂ interfaces.
For the O content and resistivity measurements, several (~800 μm thick) pieces of Si were cut longitudinally with respect to the interface after contact between the Si and SiO2 with additives, as shown in Figure 2d. Figure 11a shows the distribution of the O concentration in the Si pieces and the distance from the Si/SiO2–ceramic interface, as measured through FTIR spectroscopy. The O concentration of the Si was 10.5–13.2 × 10^{17} atoms/cm³ (12–15 ppm) before contact with the SiO2. The O concentration of the Si after contact with SiO2 decreased to ~6–9 × 10^{17} atoms/cm³, probably because of SiO evaporation during the heat treatment. However, the O concentrations of all the SiO2–ceramics were lower than those of the pure SiO2. Among them, the O concentrations of SiO2–Al2O3 and SiO2–MgO were less than 10^{16}, implying that ceramic additives in SiO2 affect the diffusion of O into the Si substrate. Figure 11b shows the electrical resistivity of the Si pieces at various distances from the interface of the Si/SiO2–ceramics, as measured using a four-point probe resistance meter. Similarly, the electrical resistivity of the Si near the interface was high and gradually decreased away from the interface for all samples. For example, the resistivity of the Si near the interface was approximately 5 Ω·cm and decreased to as low as 3 Ω·cm far from the Si/SiO2 interface. The resistivity of the Si was 21.85 Ω·cm before contact with the SiO2. As anticipated, the resistivity of the Si both near and far from the Si–ceramic interface was lower than that of pure Si. Hull [31] indicated that unintentional O diffusion into Si usually manifests as n-type doping (with SiO4 as the donor) and results in a decrease in the resistivity of Si. When Si comes into contact with SiO2, the O from the SiO2 diffuses into the Si, causing a decrease in resistivity; this is supported by our resistivity measurements shown in Figure 11b. The resistivity of the Si with all additives (0.12, 0.24, 0.21, 0.36, and 0.30 Ω·cm for Y2O3, La2O3, TiO2, Al2O3, and MgO, respectively) was less than that of the Si (~3 Ω·cm) in contact with the pure SiO2. When Al^{3+}, La^{3+}, and Y^{3+} ions diffused and replaced one or two (for Mg^{2+}) Si atoms in the substrate, the remaining valence electrons were insufficient to satisfy the four covalent neighboring bonds of the Si, resulting in the formation of holes. Thus, the Al, La, and Y(IIIA) atoms became acceptors. As for the diffusion of the Ti and the Si originating from the SiO2 into the Si substrate, the electrical property of the Si substrate could not be changed because of the charge balance effect (Si^{4+} = Ti^{4+}). However, the dissolution of Al, Mg, Y, La, Ti, Y, and O impurities in the Si substrate resulted in interstitial or vacancy defects, thus affecting the resistivity.
4. Conclusions

In summary, 10 wt% ceramics—Al₂O₃, La₂O₃, Y₂O₃, MgO, and TiO₂—were separately added to amorphous SiO₂ after pressing and annealing at 1300 °C, resulting in the amorphous SiO₂ changing to cristobalite SiO₂. The reaction phases La₂SiO₅, Y₂Si₂O₇, and MgSiO₃ (Mg₂SiO₄) in the SiO₂ with 10 wt% La₂O₃, Y₂O₃, and MgO additives were identified through XRD, SEM, and TEM. After Si came into contact with SiO₂—ceramics, observed by SEM and TEM, two types of microstructures were found: those with and those without an amorphous SiO₂ reaction layer at the interface. No reaction layer was found with the La₂O₃, Y₂O₃, and MgO additives; by contrast, a reaction layer was found with the Al₂O₃ and TiO₂ additives. The formation of the amorphous SiO₂ reaction layer was due to the substitution of the Si position of the SiO₂ with Al³⁺ and Ti⁴⁺ impurities, which can break the bonds between Si atoms. The O content in the Si far from the interface decreased to 6–9 × 10¹⁷ atoms/cm³ for pure SiO₂ and less than 10¹⁶ atoms/cm³ for SiO₂–Al₂O₃ and SiO₂–MgO, implying that ceramic additives in SiO₂ affect the diffusion of O into the Si substrate. The resistivity of the Si in the SiO₂ decreased from 3 to 0.12–0.36 Ω·cm with the ceramic additives using a four-point probe resistance meter due to charge balance effect.

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