



Effect of Zr doping on the high-temperature stability of SiO₂ glass

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ABSTRACT

A SiO₂–ZrO₂ glass was prepared by cold pressing and sintering, and the effect of ZrO₂ on the high-temperature stability of SiO₂ was studied. First-principle calculation based on density functional theory was applied to analyze the solution energies of Zr atom in ZrSiO₄ and SiO₂. The results show that Zr element can diffuse into SiO₂ lattice, and influence the SiO₂ structure in two ways, including introduction in the interstitial region and substituting a Si atom in SiO₂. The interstitial Zr breaks the nearest Si–O bond to form Zr–O and Zr–Si bonds, while the substitutional Zr has little influence on the SiO₂ network. The interfacial adhesion energy between the Zr-doped SiO₂ and the pure SiO₂ increases from 3.93 J/m² to 4.56 J/m² with the introduction of Zr atom, which is beneficial for improving the high-temperature stability of SiO₂ glass.

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1. Introduction

Recently, SiC has attracted considerable attention as oxidation resistant coatings to protect carbon/carbon (C/C) composites for applications in high-temperature oxygen-containing environments due to its high melting point, low coefficient of thermal expansion (CTE), excellent thermal shock resistance and high temperature oxidation resistance [1–3]. The excellent oxidation resistance of SiC is attributed to the produced SiO₂ glass at high-temperature oxygen-containing atmosphere, which has extremely low oxygen permeability (1.4×10^{-17} m²/s at 1200 °C), and can effectively prevent oxygen from diffusing further into the substrate [4]. However, the oxidation resistance of single SiC is still not high enough for some severe applications due to the volatilization of SiO₂ [5]. To further improve the oxidation resistance of SiC, ultrahigh temperature ceramics (UHTCs) such as Zr-based compounds (ZrB₂, ZrC), with the excellent thermochemical properties [6,7], were usually added in SiC coatings [8,9]. For example, Ren et al. [10] prepared ZrB₂–SiC gradient coating on C/C composites and stated that the oxidation resistance of SiC coating could be improved by the addition of ZrB₂, explaining that the softening temperature of SiO₂ glass would increase with Zr addition. The similar phenomenon was also found by Li et al. in their research on SiC–ZrB₂–ZrC coating [11,12]. However, the theoretical investigation of Zr–SiO₂ interaction is lacked. Moreover, the interfacial adhesion between

Zr-doped SiO₂ and pure SiO₂ should have positive role on the thermal stability of SiO₂ glass, which is also worth exploring.

In the present work, a dense SiO₂–ZrO₂ glass was prepared by cold pressing and sintering. First-principle method was applied to investigate the effect of Zr atom on the characteristics of SiO₂ lattice and the interface between Zr-doped SiO₂ and SiO₂ in theory.

2. Procedures

2.1. Experiment

SiO₂–ZrO₂ glass was prepared by cold pressing and sintering. Firstly, B₂O₃ (amorphous phase, purity: 99.90%) and SiO₂ (amorphous phase, purity: 99.99%) powders were mixed with the mass ratio of 1:49. The proper amount of B₂O₃ was added to obtain dense glass sample. ZrO₂ powders (tetragonal phase, purity: 99.00%) were introduced into the mixture with the content of 5, 10 and 15 wt%. Subsequently, the mixed powder was pressed at a pressure of 60 MPa for 100 s followed by heating at 1773 K for 2 h in air. For comparison, the SiO₂ glass without ZrO₂ in raw materials was prepared by the same process. The morphology and element distribution of the glass were analyzed by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). The crystalline structure of the samples was measured by X-ray diffraction (XRD).

SiO₂–ZrO₂ glass samples with a size of 15 mm × 15 mm × 4 mm were used to test the volatility in air in a corundum tube furnace. After heat treatment at 1873 K for 5 h, the samples were naturally cooled to room temperature in the furnace. Mass loss percentages

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($\Delta M\%$) of the glass sheets were calculated by the following equation:

$$\Delta M\% = \frac{(m_0 - m_1)}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 were the masses of the glass sheets before and after heat treatment, respectively [11].

2.2. Model

First-principle calculation based on density functional theory (DFT) with the CA-PZ local density approximation (LDA) method by CASTEP code was used [13]. Broyden-Fletcher-Goldfarb-Shanno (BFGS) and ultrasoft pseudopotentials were also employed. The energy cut-off for the basis set was 400 eV, which was sufficient for the total energy and geometry of SiO_2 and Zr-doped SiO_2 supercell. Brillouin zone was done using the Monkhorst-Pack scheme in the relevant irreducible wedge [14]. Geometry within the unit cell was optimized to the absolute value of force on each unconstrained atom < 0.001 eV/Å. Mulliken bond populations with 3.0 Å distance cut-off were calculated to explain the bond strength. A cristobalite phase was used to evaluate the influence of Zr on the characteristics of SiO_2 , which has been adopted by other researches [13,15].

To study the stability of Zr atom in the surface of ZrSiO_4 and SiO_2 , ZrSiO_4 (0 0 1) and SiO_2 (0 0 1) were chosen considering their low lattice misfit (only 3.6%) for a lateral cell of 188 \AA^2 . Since it is difficult to calculate the interfacial reaction between ZrSiO_4 (0 0 1) and SiO_2 (0 0 1) due to the large interfacial area, the solution behavior of Zr atom in ZrSiO_4 (0 0 1) with a Zr vacancy (Fig. 1(a)) and SiO_2 (0 0 1) (Fig. 1(b)) were separately calculated by Eqs. (2) and (3) [16].

To model ZrSiO_4 (0 0 1) with a Zr vacancy, a 15 Å vacuum layer and an eight-layer single-Zr-terminated ZrSiO_4 (0 0 1) slab were used. The bottom four-substrate layers were kept fixed at their bulk positions. For SiO_2 (0 0 1) slab, a same vacuum layer and a six-layer single-O-terminated configuration were structured. The bottom three-substrate layers were kept fixed at their bulk positions.

$$E_{\text{ZrSiO}_4(001)}^s = E_{\text{ZrSiO}_4(001)} - E_{\text{ZrSiO}_4(001) \text{ with a Zr vacancy}} - E_{\text{Zr}}, \quad (2)$$

$$E_{\text{SiO}_2+\text{Zr}(001)}^s = E_{\text{SiO}_2+\text{Zr}(001)} - E_{\text{SiO}_2(001)} - E_{\text{Zr}}, \quad (3)$$

where $E_{\text{ZrSiO}_4(001)}$ and $E_{\text{ZrSiO}_4(001) \text{ with a Zr vacancy}}$ were the energies of perfect ZrSiO_4 (0 0 1) and ZrSiO_4 (0 0 1) with a Zr vacancy, respectively. $E_{\text{SiO}_2+\text{Zr}(001)}$ and $E_{\text{SiO}_2(001)}$ were the energies of SiO_2 (0 0 1) with an interstitial Zr and perfect SiO_2 (0 0 1), respectively. E_{Zr} denoted the chemical potential of Zr atom.

The solution energy of an interstitial or substitutional Zr atom in SiO_2 lattice was written as following:

$$E_{\text{in-Zr}}^s = E_{\text{SiO}_2+\text{in-Zr}} - E_{\text{SiO}_2} - E_{\text{Zr}}, \quad (4)$$

$$E_{\text{su-Zr}}^s = E_{\text{SiO}_2+\text{su-Zr}} - E_{\text{SiO}_2} - E_{\text{Zr}} + E_{\text{Si}}. \quad (5)$$

where $E_{\text{SiO}_2+\text{in-Zr}}$ and $E_{\text{SiO}_2+\text{su-Zr}}$ were the energies of the SiO_2 system with an interstitial or substitutional Zr, respectively. E_{SiO_2} and E_{Si} denoted the energy of the pure SiO_2 system and the chemical potential of Si atom, respectively.

The ideal adhesion energy was defined as:

$$E_{\text{adh}} = (E_{\text{sub}} + E_{\text{coat}} - E_{\text{int}}) / 2A. \quad (6)$$

where E_{sub} and E_{coat} were the total energies of the isolated pure SiO_2 substrate and Zr-doped SiO_2 slabs, respectively. The term E_{int} represented the total energy of the system when the pure SiO_2 substrate and the Zr-doped SiO_2 surfaces were allowed to come together and adhere at equilibrium separation [17]. A was the area. In the present work, the SiO_2 structural model was constructed according to the work of Wang et al. [15], where a SiO_2 slab of three O–Si–O layers well represented a thin film of SiO_2 . Thus, in this work, a structurally converged thickness of three O–Si–O layers for Zr-doped SiO_2 film and a six-layer SiO_2 (0 0 1) slab for substrate were built. The bottom three substrate layers were kept fixed at their bulk positions. The bottom surface of Zr-doped SiO_2 film was comprised of O atom with one unpaired electron, which would interact with the surface Si layer of SiO_2 (0 0 1). The interface space was about 2.0 Å and vacuum layer was 10 Å. A $4 \times 4 \times 1$ k-mesh was used for the interface, which converged the adhesion energy to ~ 0.01 J/m². Since the surface energy was not well-defined for a doped SiO_2 surface, here the interfacial binding energy was estimated by comparing the relaxed structures at the same thicknesses [15]. Therefore, the same vacuum layer thickness and k-mesh were also used for the isolated Zr-doped SiO_2 (1 1 0), and pure SiO_2 (0 0 1) surfaces.

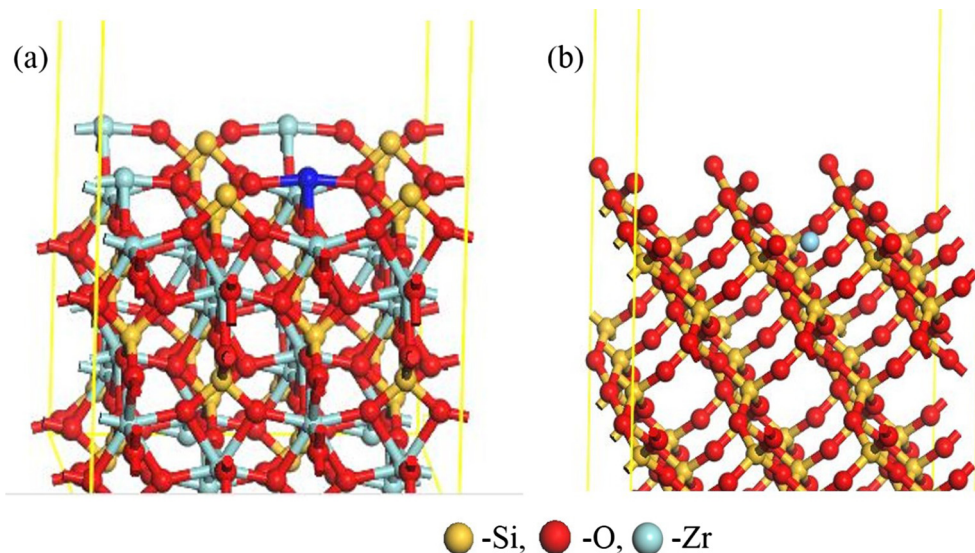


Fig. 1. Bulk structures of (a) ZrSiO_4 and (b) SiO_2 with an interstitial Zr impurity. The navy blue sphere denotes the location of Zr vacancy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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