Introduction

Determination of pH value is one of the most important measurements in all pH dependent chemical processes, especially in agricultural development, biochemical technology, the pharmaceutical industry, and corrosion control areas. Currently, the most often used electrode is a traditional glass electrode. However, glass electrodes have two main problems, namely the fragility of the glass membrane and low sensitivity to interfering species. Glass electrodes have two main problems, namely the fragility of the glass membrane and low sensitivity to interfering species. In the paper, we developed a high-performance solid-state pH sensor using a Ce0.9Sr0.1(Zr0.53Ti0.47)O4 (CSZT) membrane through a very simple gel-spin-coating process. The structural properties of the CSZT membrane are correlated with its sensing characteristics. The CSZT based EIS sensor exhibited high pH sensitivity of 92.48 mV pH⁻¹, which is beyond the Nernst limit (59.4 mV pH⁻¹), and good reliability in terms of a low hysteresis voltage of 1 mV and a small drift rate of 0.15 mV h⁻¹. This behaviour is attributed to the incorporation of Sr in the CSZT sensing membrane, which promotes change in the Ce oxidation state from Ce⁴⁺ to Ce³⁺.

Experimental

The CSZT mixed oxide membrane was synthesized with 1 N HNO₃ and CH₃COOH via a simple sol-gel method. The cerium acetate hydrate, strontium nitrate, zirconium propoxide, and titanium isopropoxide were mixed according to the molar ratio of Ce : Sr : Zr : Ti = 0.9 : 0.1 : 0.53 : 0.47. To adjust the concentration to 0.2 M with a total volume of 20 ml, acetic acid was used. After cleaning the 4-in p-type (100) Si wafer through a standard RCA process, the CSZT sensing membrane was
Results and discussion

Fig. 1(a) shows the X-ray diffraction (XRD) data of the CSZT membrane. The well-defined plane of (101) at 2θ = 29.15° is found in the XRD pattern, and is indicative of the fluorite-type tetragonal structure. In addition, the (101) peak position of the CSZT membrane was shifted to a lower 2θ value and the d spacing became higher (3.06 Å) relative to those of the Ce0.5Zr0.5O2 reference (JCPDS card no. 00-038-1436). This behaviour is mainly due to the higher ionic radii of the Ti and Sr incorporated into the CSZT membrane. Fig. 1(b) displays the atomic force microscopy (AFM) surface morphology image of the CSZT membrane. The surface roughness was estimated to be 0.39 nm. Fig. 2 displays the XPS spectra of (a) Ce 3d, (b) Sr 3d, (c) Zr 3d, (d) Ti 2p, and (e) O 1s for the CSZT membrane. The Ce 3d, Sr 3d, Zr 3d, Ti 2p, and O 1s element peaks were fitted using a combined symmetric Gaussian-Lorentzian line shape function after a Shirley background subtraction, except for the Ce 3d peak (linear background). Fig. 2(a) demonstrates that the Ce 3d spectra can be deconvoluted into eight peaks: \( \nu \) (882.6 eV), \( \nu' \) (884.9 eV), \( \nu'' \) (888.7 eV), \( \nu''' \) (898.1 eV), \( \mu \) (900.4 eV), \( \mu' \) (902.7 eV), \( \mu'' \) (907.2 eV), and \( \mu''' \) (916.5 eV). The four bands of \( \mu \) and those of \( \nu \) represent Ce 3d\(_{5/2}\) and 3d\(_{3/2}\), respectively. The peaks of \( \nu \) and \( \mu \), \( \nu' \) and \( \mu' \), and \( \nu'' \) and \( \mu'' \) can be assigned to the \((3d^34f^3),(3d^34f^4)O(2p^5)\), and \((3d^34f^5)O(2p^6)\) states of Ce\(^{4+}\), respectively, whereas the \((3d^34f^4)O(2p^5)\) state of Ce\(^{3+}\) can be allotted to \( \nu \) and \( \mu \). The ratio of Ce\(^{3+}\) to total Ce (namely, Ce\(^{4+}\) + Ce\(^{3+}\)) is 21.36% higher than in previous studies [19.5% for Ce\(_x\)(Zr\(_{53}\)Ti\(_{47}\))O\(_{4}\) (CZT) film without Sr component]. This is ascribed to the Sr incorporated into the CSZT membrane enhancing the change from Ce\(^{4+}\) to Ce\(^{3+}\) in the Ce oxidation state. Fig. 2(b) depicts that the Sr 3d\(_{3/2}\) and 3d\(_{5/2}\) double peaks at 134.8 eV and 133.1 eV, respectively, for the CSZT membrane are shifted toward higher binding energies compared with those of the SrTiO\(_3\) reference. The higher Sr 3d double binding energies of the CSZT film may be attributed to a mixture of Sr\(^{2+}\) ions in the CeO\(_2\) lattice. In addition, the ionic radius of Ce\(^{4+}\) (0.99 Å) is larger than that of Ti\(^{4+}\) (0.74 Å). Moreover, there is a shift in the Zr 3d\(_{3/2}\) and 3d\(_{5/2}\) split peaks (184.1 and 181.8 eV, respectively) to binding energies that are lower relative to those of ZrO\(_2\) film (185.8 and 182.2 eV, respectively), indicating the formation of Ce–Sr–O–Zr–Ti bonds. Fig. 2(e) demonstrates that the O 1s spectra of the CSZT membrane were convoluted with three appropriate curve-fitting lines. For the three spectra, the first peak at 531.4 eV represents Ce(OH)\(_3\), the second peak at 530 eV indicates the Ce\(^{3+}\) state, and...
the third peak at 529.1 eV indicates the Ce4+ state.23,24 The intensity of the O 1s peak corresponding to the Ce2O3 component is lower than that of CeO2, but is higher relative to our previous reports (the CZT film).25 Fig. 2(f) shows the HR-TEM image of the CSZT membrane. The oxide thickness of the CSZT membrane was evaluated to be ~47 nm.

Fig. 3(a) shows the C–V plots of the CSZT EIS sensor annealed at 800 °C for standard buffer solutions. To measure the sensitivity of the EIS device the shift in reference voltage (VREF), as shown in the C–V plots, was measured as it changes with the pH of the buffer solution due to mainly protonation or deprotonation which modifies the surface potential through dipole formation on the sensing membrane. Fig. 3(b) presents the VREF of the CSZT EIS sensor as a function of pH. The CSZT EIS sensor exhibited a super-Nernstian pH sensitivity of 92.48 mV pH−1 with a linear response in the range of pH 2–12, which is far larger than the theoretical Nernstian value (59.4 mV pH−1 at 25 °C). This super-Nernstian response may be attributed to the incorporation of Sr into the CSZT film, which enhances the change in the Ce oxidation state from Ce4+ to Ce3+. In this case, we could suspect that in a mild solution, the oxidized Ce4+ and reduced Ce3+ ion participate in the redox reactions below:

$$\text{Ce(OH)}_3 \leftrightarrow \text{Ce(OH}_2\text{O}_2^{-} + \text{H}^{+} \quad (1)$$

$$\text{Ce}_2\text{O(OH)}_6 \leftrightarrow \text{Ce}_2\text{O(OH)}_2\text{O}_4^{4-} + 4\text{H}^{+} \quad (2)$$

$$2\text{Ce(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ce}_2\text{O(OH)}_6 + 2\text{H}^{+} + 2\text{e}^{-} \quad (3)$$

Substituting eqn (1) and (2) into (3), we can obtain the stoichiometric redox reaction:

$$2\text{Ce(OH)}_2\text{O}^{-} + \text{H}_2\text{O} \leftrightarrow \text{Ce}_2\text{O(OH)}_2\text{O}_4^{4-} + 4\text{H}^{+} + 2\text{e}^{-} \quad (4)$$

From this reaction, only two electrons are transferred per four protons (proton/electron ratio of 2), hence a sensitivity of 118.8 mV pH−1 was achieved because of the mixing of the oxidized CeO2 and reduced Ce2O3 states in the CSZT membrane. The empirical result of the pH sensitivity being over 59.4 mV pH−1 can be explained by there being less than one electron per proton transferred in the redox reaction. In contrast, the pH sensitivity being below 59.4 mV pH−1 might be due to there being more than one electron per proton transferred in this reaction.

To evaluate the hysteresis of the CSZT EIS sensor, it was subjected to two pH loops of 7 → 4 → 7 → 10 → 7 and 7 → 10 → 7 → 4 → 7 over a period of 1500 s, as shown in Fig. 4(a). The hysteresis voltages were estimated to be 1 and 1.5 mV for the 7 → 4 → 7 → 10 → 7 and 7 → 10 → 7 → 4 → 7 loops, respectively. The smaller hysteresis of the CSZT film is attributed to the formation of a CSZT stoichiometric structure, thus leading to minimal buried oxide. Fig. 4(b) demonstrates the drift rate of an EIS sensor measured at pH 4, 7 and 10 for 12 h. The CSZT EIS sensor exhibited a low drift rate of 0.15 mV h−1 at pH 7. In this study, our CSZT membrane demonstrated a pH detection sensitivity (92.48 mV pH−1) that is superior to those of materials commonly used for EIS or ISFET-based sensors, such as Al2O3 (58 mV pH−1), TiO2 (55 mV pH−1), Ta2O5 (56–58 mV pH−1), ZrO2 (~55 mV pH−1), HfO2 (~55 mV pH−1), Y2O3 (54.5 mV pH−1), and CZT (64.42 mV pH−1).26

**Conclusions**

In summary, we have demonstrated a high-performance CSZT membrane deposited on a Si substrate through a simple sol–gel spin-coating process. A high pH sensitivity of 92.48 mV pH−1, a small hysteresis voltage of 1 mV, and a low drift rate of 0.15 mV h−1 were achieved by the CSZT EIS sensor. These results are attributed to the incorporation of Sr in the CSZT, which enhances the change in the Ce oxidation state from Ce4+ to Ce3+, resulting in a rise in the ratio of protons to electrons transferred in the redox reaction. This CSZT membrane EIS sensor can be used in future solid-state biosensor devices.

**Conflicts of interest**

There no conflicts to declare.

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**References**