In this study, CeO₂ pH-sensitive sensing membranes in electrolyte-insulator-semiconductor structures on silicon substrate were fabricated. To enhance sensing performance, the membrane underwent Ti doping and NH₃ plasma treatment on the surface. To examine the effects of Ti doping and plasma treatment, multiple material properties evaluations were conducted using field-emission scanning electron microscopy, X-ray diffraction, atomic force microscopy, and secondary ion mass spectroscopy. Results indicate that Ti doping and plasma treatment can remove defects and enhance crystallization, thereby achieving improved pH-sensing performance of the membrane with high sensitivity, high linearity, low hysteresis voltage and low drift voltage. CeO₂-based EIS membranes with Ti doping and NH₃ plasma treatment show promise for future portable pH-sensitive biosensors.

Within this decade, pH-sensing technologies have been intensively studied for biochemical applications. This is due in large part to the fact that pH value is key to the health of living organisms, influencing function, development and growth of living systems. In the early 20th century, researchers have used colorimetric and electrometric methods to examine the pH values in different solutions by observing their colors and measuring their voltage variations. Since then, light detection and voltage detection have become two distinct methods by which to carry out pH sensing. For pH sensing using the light detection approach, optical fibers were utilized to monitor color changes of the dye in solutions in the 1980s. Recently, Li et al. used detection of fluorescent light absorption related to energy level variations to evaluate pH values. Alternately, detection of voltage variation from a semiconductor device began from 1970, when Bergveld invented the first ion-sensitive field effect transistor (ISFET). An ISFET is derived from a metal oxide semiconductor field effect transistor with an ion-sensing gate structure, in contact with a buffer solution. In the 1990s an electrolyte-insulator-semiconductor (EIS) structure was invented using a sandwiched insulating sensing membrane in contact with an electrolyte on top and a semiconductor on the bottom. EIS biosensing devices have been attracting intensive attention because of their rapid response, robustness, compact size, and possible integration with an on-chip circuit. Over the past decade, various types of metal oxides such as Nb₂O₅, HfO₂, and TiO₂ have been used as the sensing insulator in an EIS structure. Recently, some rare earth oxides, with advantages including wide band gaps, large band offsets on Si, and high dielectric constants have been demonstrated as good sensing insulators for EIS biosensing devices. Among these rare earth oxides, CeO₂ with a wide bandgap of 3.19 eV and a high dielectric constant, has been used as the sensing material for EIS biosensing devices. In addition, Kao et al. have proposed the positive effects of annealing on the CeO₂ membrane in 2014, and the influence of CF₄ plasma treatment on the CeO₂ sensing insulator in 2015. However, to further improve the material properties of the sensing membrane and hence boost the sensing capability, alternative processes or distinctive treatments are worth exploration and investigation. In addition to the conventional thermal annealing treatment, incorporation of atoms during membrane layering by co-sputtering or the addition of different atoms after membrane deposition with plasma treatment have been
proposed to reinforce the membrane in order to reducing defects. Recently, the incorporation of Ti atoms\textsuperscript{20} and NH\textsubscript{3} plasma treatment\textsuperscript{21} have been utilized to improve the sensing membrane performance. Based on the previous report\textsuperscript{20}, Ti doping in the insulator layer can fix defects in the membrane\textsuperscript{22}. Furthermore, addition of N atoms through the NH\textsubscript{3} plasma treatment on the surface of the sensing insulator can mitigate dangling bonds on the membrane surface and hence ameliorate the solution/insulator interface during the sensing operation\textsuperscript{23,24}. In this paper, we combined Ti doping and NH\textsubscript{3} plasma treatment to optimize the sensing performance of the membrane.

In this research, Ce\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} membrane-based EIS biosensors were fabricated with Ti doping into the membrane by cosputtering and N-atom incorporation by NH\textsubscript{3} plasma treatment on the surface of the membrane. Moreover, multiple material analyses, including secondary ion mass spectroscopy (SIMS), field-emission scanning electron microscopy (FESEM), and X-ray photoelectron spectroscopy (XPS), were conducted to investigate the composition and surface characteristics of the membrane.

**Figure 1.** The Ce\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} EIS structure.

**Figure 2.** FESEM images of (a) the as-deposited CeO\textsubscript{2} sample (b) the Ce\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} sample (c) the as-deposited CeO\textsubscript{2} sample with NH\textsubscript{3} plasma treatment for 3 min (d) the Ce\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} sample with NH\textsubscript{3} plasma treatment for 3 min.
microscopy (FESEM), X-ray diffraction (XRD), and atomic force microscopy (AFM) were performed to study the improvements of material properties caused by Ti doping and NH$_3$ plasma treatment. SIMS results show that the piling up of N atoms may fix interfacial dangling bonds. Moreover, FESEM images clearly indicate that both Ti doping and NH$_3$ plasma treatment can enhance granization. Consistent with the FESEM images and XRD analysis, AFM images reveal that incorporation of Ti atoms can reinforce the crystallization of the CeO$_2$ insulator. In addition, the pH-sensing sensing capabilities were measured$^{25,26}$. In line with the material analysis, results indicate that incorporation of Ti doping and NH$_3$ plasma treatments could effectively improve pH sensing behavior and sensing capability. The Ti-doped NH$_3$ plasma treated EIS biosensors have the potential to develop future portable biochemical sensors at an industrial level.

**Results and Discussion**
The detailed EIS structure is illustrated in Fig. 1. Material analyses were performed on the membrane film and sensing measurements were conducted on the EIS sensors. To characterize the influence of Ti addition and NH$_3$ plasma treatment on the CeO$_2$ membrane, multiple material characterizations including FESEM, XRD, AFM, and SIMS were performed on CeO$_2$ and Ce$_2$Ti$_2$O$_7$ films with and without NH$_3$ plasma treatment. First, we used FESEM to view the surface morphologies of CeO$_2$ and Ce$_2$Ti$_2$O$_7$ films as shown in Fig. 2(a,b,c and d). An FESEM

![XRD Image](image1)

Figure 3. XRD of (a) CeO$_2$ samples with NH$_3$ plasma treatment in various conditions. (b) Ce$_2$Ti$_2$O$_7$ samples with NH$_3$ plasma treatment for 3 min.

![AFM Images](image2)

Figure 4. AFM images of the CeO$_2$ sample without NH$_3$ plasma treatment and with NH$_3$ plasma treatment for 3 min. The normalized C-V curve of the Ce$_2$Ti$_2$O$_7$ sample without and with NH$_3$ plasma treatment for 3 min.
image of the as-deposited CeO\(_2\) film is shown in Fig. 2(a). Compared with the as-deposited CeO\(_2\) film, the FESEM image of the Ti-doped CeO\(_2\) film without NH\(_3\) plasma treatment as shown in Fig. 2(b) reveals that clearer nano-grains could be observed, indicating that Ti addition might reinforce crystallization. Similarly, the CeO\(_2\) film treated with NH\(_3\) plasma as shown in Fig. 2(c) exhibited clearer grain images than the CeO\(_2\) as-deposited film, showing that NH\(_3\) plasma treatment could enhance crystallization as well. Furthermore, CeO\(_2\) film incorporating Ti atoms with NH\(_3\) plasma treatment as shown in Fig. 2(d) exhibited the strongest crystallization among all the samples. In addition, slight cracks around the grains might further enhance the contact area in the membrane/electrolyte surface and boost the sensing performance.

Additionally, we used XRD to examine the CeO\(_2\) films and the Ce\(_2\)Ti\(_2\)O\(_7\) films incorporated with Ti atoms in various NH\(_3\) plasma treatment conditions, as shown in Fig. 3(a and b). Consistent with the FESEM images as
shown in Fig. 2(a,b,c and d). XRD patterns reveal that NH₃ plasma treatment for 3 min could drastically enhance the CeO₂ (400) peak and the CeO₂ (200) peak intensity indicative of crystallization during NH₃ plasma treatment. Furthermore, Ti addition could cause CeO₂ crystals to form Ce₂Ti₂O₇ crystals as shown in Fig. 3(b). Furthermore, NH₃ plasma treatment for 3 min could increase crystallization as 3 min NH₃ plasma treatment increased the Ce₂Ti₂O₇ (2,2,1) peak and the Ce₂Ti₂O₇ (2,1,2) peak drastically. The results show that Ti addition and NH₃ plasma treatment could effectively strengthen crystallization and hence improve the sensing performance of the CeO₂ membrane.

In addition, AFM images as shown in Fig. 4 reveal that the surface roughness of the CeO₂ and Ce₂Ti₂O₇ films treated in various NH₃ plasma conditions. Compared with the CeO₂ film and Ce₂Ti₂O₇ as shown in Fig. 4, Ti doping could effectively increase the surface roughness and cause the grain on the surface to become more noticeable. Similarly, NH₃ plasma treatment could increase roughness and cause grain growth as well. Moreover, incorporating both Ti doping and NH₃ plasma treatment for 3 min could drastically increase the roughness from 0.424 nm to 0.815 nm and clearly enhance the grains, as shown in the AFM images.

Furthermore, SIMS analysis as shown in Fig. 5 reveals the distribution of various atoms inside the CeO₂/Si film and the Ce₂Ti₂O₇/Si films. Figure 5 shows stronger N atom concentrations in both the CeO₂ film and the Ce₂Ti₂O₇ film after NH₃ plasma treatment. Moreover, noticeable accumulation could be observed in the membrane/Si interface. Since NH₃ plasma treatment could infuse N atoms into the CeO₂ and Ce₂Ti₂O₇ films, stronger N-Ce and N-Si bonds might be formed and dangling bonds or defects around the interface might be fixed. Strengthening the material quality in the bulk and in the interface might increase the sensitivity and linearity of pH sensing of the films. Furthermore, a high concentration of Ti atoms in the SIMS profile for the Ce₂Ti₂O₇ films could be observed. Since Ti addition could also fix traps and dangling bonds, a high concentration of Ti atoms in the Ti-doped CeO₂ film could cause the Ti atoms to reduce the defects. In addition, a slight increase of concentration of Ti atoms might indicate the accumulation of the Ti atoms around the interface and fix the dangling bonds near the interface.

Incorporating a CeO₂ membrane as the electroactive gate film in the pH-based EIS structure allows the incorporated sensor to detect fine pH value variations. The influence of the plasma treatment and Ti doping can be realized by studying the site binding model. The reference voltage is closely related to the surface potential, which is dependent on the pH value of the electrolyte and the membrane material.

\[
\psi = 2.303 \frac{kT}{q} \beta \frac{\beta + 1}{(pH_{\text{ref}} - pH)}
\]  

(1)
The $\varphi$ value can be calculated from the above equation (1), where $k$ is the Boltzmann's constant, $T$ is the temperature, and $\beta$ is a parameter in terms of the chemical sensitivity of the membrane. The value of $\beta$ is proportional to the density of surface hydroxyl groups and is determined by the following equation (2).

$$\beta = \frac{2q^2 N_s \sqrt{K_{a} K_{b}}}{K_{\text{DL}}}$$  (2)

$N_s$ is the number of surface sites per unit area. $K_{a}$ is the equilibrium constant of the acid point and $K_{b}$ is the equilibrium constant of the base point, respectively. $C_{\text{DL}}$ is the bilayer capacitance calculated from the Gouy-Chapman-Stern model.

According to the above theories, addition of Ti atoms and incorporation of NH$_3$ plasma treatment could enhance crystallization and reduce the dangling bonds. Therefore, the number of the surface sites could be increased and the sensing performance could be boosted. To characterize the sensing performance of the CeO$_2$ and Ce$_2$TiO$_7$ membranes with and without NH$_3$ plasma treatment, the C-V curves of these various membranes are shown in Fig. 6(a,b,c and d). The linearity and sensitivity of the CeO$_2$ and Ce$_2$TiO$_7$ membranes with and without NH$_3$ plasma treatment extracted from normalized C-V curve are shown in Fig. 7(a,b,c and d). As shown in Fig. 6(a) and 7(a), the as-deposited CeO$_2$ membrane exhibited a low sensitivity of 34.37 mV/pH. Moreover, fluctuated C-V curves could be observed indicating multi-capacitance effects were present, signifying that defects in the bulk or in the interface might be present. As the membrane underwent the NH$_3$ plasma treatment for 3 min, the sensitivity was boosted to 48.62 mV/pH and the C-V curves became smoother as shown in Figs 6(b) and 7(b). Similarly, as the as-deposited CeO$_2$ membrane and the as-deposited Ce$_2$TiO$_7$ membrane were compared as shown in Fig. 7(a and c), the sensitivity was improved when the Ti atoms were incorporated into the CeO$_2$ membrane.

Figure 8. The hysteresis of (a) CeO$_2$ and (b) Ce$_2$TiO$_7$ sensing membrane with NH$_3$ plasma treatment in various conditions during a pH loop of 7 → 4 → 7 → 10 → 7 over a period of 25 minutes.
Furthermore, as the Ce₂TiO₇ membrane went through NH₃ plasma treatment for 3 min, the sensitivity was greatly improved to 54.43 mV/pH. Furthermore, much smoother C-V curves could be observed, indicating single capacitance with high material quality film could be formed. Combining Ti doping and NH₃ plasma treatment could enhance the CeO₂ film material quality and sensing capability.

Furthermore, to study the hysteresis effects of the CeO₂ and Ce₂TiO₇ films which underwent through various plasma treatment conditions, hysteresis voltages were measured for the CeO₂ film and the Ce₂TiO₇ film with different plasma treatment conditions, as shown in Fig. 8(a and b). The as-deposited CeO₂ film with a hysteresis voltage of 27.7 mV and the as-deposited Ce₂TiO₇ film with a hysteresis voltage of 20.8 mV could be observed, indicating that Ti-doping might reduce the dangling bonds and traps to lower the hysteresis voltage. Furthermore, the CeO₂ with NH₃ plasma treatment had a low hysteresis voltage of 7.8 mV, and the Ce₂TiO₇ film with NH₃ plasma voltage had the lowest hysteresis voltage of 5.6 mV. The results indicate that NH₃ plasma treatment could passivate defects and enhance sensing performance, consistent with the material analysis.

Finally, the CeO₂ membrane and the Ce₂TiO₇ membrane prepared in different plasma treatment conditions were tested for gate drift voltage, as shown in Fig. 9(a and b). Each of the samples were dipped in a pH7 buffer solution. In line with all the previous analyses, results reveal that the drift voltage shift could be reduced either by Ti doping or NH₃ plasma treatment for 3 min. Moreover, the Ce₂TiO₇ membrane with NH₃ plasma treatment had the least drift voltage of 0.21 mV/hr, signifying that Ti doping combined with NH₃ plasma treatment could effectively enhance sensing capability. Moreover, to compare EIS membranes composed of various materials and treated with different treatment, the EIS pH biosensing devices incorporating ZnO, Gd₂O₃, Gd₂TiO₇ and Nb₂O₅ membranes are compared with CeO₂ and Ce₂TiO₇ membranes as shown in Table 1.32–34.

![Figure 9. The drift voltage of (a) CeO₂ and (b) Ce₂TiO₇ sensing membrane with NH₃ plasma treatment in various conditions and then dipped in pH7 buffer solution for 12 hours.](image-url)
8. Schöning, M. J. “Playing around” with field-effect sensors on the basis of EIS structures.
9. Kao, C.-H. and the hysteresis and the drift voltage could be reduced. CeO₂-based EIS membranes with Ti doping and NH₃ fabricated on 4 inch n-type (100) silicon wafers with a resistivity of 5–10 Ω-cm. After standard RCA cleaning, the

Table 1. Comparison with pH sensing devices composed of various membranes with different treatments. (RTA: rapid thermal annealing. CF₄: CF₄ plasma treatment. NH₃: NH₃ plasma treatment).

| Sensing membrane            | pH sensitivity (mV/pH) | Hysteresis voltage (mV) | Drift rate (mV/h) |
|-----------------------------|------------------------|-------------------------|-------------------|
| ZnO with RTA                | 42.54                  | 7.37                    | 1.78              |
| Nb₂O₅ with CF₄              | 52.15                  | 5.22                    | 3.34              |
| Gd₂O₃ with RTA              | 48.29                  | 5.8                     | 2.2               |
| Gd,TiO₂ with RTA            | 55.27                  | 3.6                     | 1.37              |
| CeO₂                        | 34.37                  | 27.7                    | 9.91              |
| CeO₂ with NH₃               | 48.62                  | 7.8                     | 0.51              |
| Ce₂TiO₇                     | 37.79                  | 20.8                    | 5.81              |
| Ce₂TiO₇ with NH₃            | 52.43                  | 5.6                     | 0.21              |
| Gd₂O₃ with CF₄              | 54.37                  | 27.7                    | 9.91              |
| Gd₂O₃ with NH₃              | 48.62                  | 7.8                     | 0.51              |
| Ce₂TiO₇                     | 37.79                  | 20.8                    | 5.81              |
| Ce₂TiO₇ with NH₃            | 52.43                  | 5.6                     | 0.21              |

Conclusions
In this study, CeO₂ EIS biosensors incorporated Ti doping and NH₃ plasma treatment were fabricated. Multiple material analyses suggest that the addition of Ti atoms to form Ce₆Ti₇O₂₇ film could enhance grain growth and suppress dangling bonds. Furthermore, inclusion of N atoms by NH₃ plasma treatment could reinforce crystallization and remove defects. Therefore, the sensitivity and linearity of the CeO₂ EIS biosensor might be boosted and the hysteresis and the drift voltage could be reduced. CeO₂-based EIS membranes with Ti doping and NH₃ plasma treatment show promise for future industrial biosensing applications.

Methods
Electrolyte-insulator-semiconductor (EIS) structures incorporating CeO₂ and Ce₂TiO₇ sensing membranes were fabricated on 4 inch n-type (100) silicon wafers with a resistivity of 5–10 Ω-cm. After standard RCA cleaning, the samples were dipped into 1% hydrofluoric acid to etch native oxide from the surface. For the first type of samples, a 50 nm CeO₂ film was deposited on the Si substrate by reactive radio frequency (rf) sputtering from a cerium target and a titanium target in diluted O₂ ambient (Ar/O₂ = 25 sccm/0 sccm). For the second group of samples, a 50 nm Ce₆Ti₇O₂₇ sensing film was deposited by reactive radio frequency (rf) co-sputtering on an n-type silicon wafer, sputtered from a cerium target and a titanium target in diluted O₂ ambient (Ar/O₂ = 20 sccm/5 sccm). The rf power and chamber pressure were 100 W and 20 mTorr, respectively. After deposition, CeO₂ and Ce₂TiO₇ were subjected to a post-NH₃ plasma treatment in a plasma-enhanced chemical vapor deposition (PECVD) system with rf power of 30 W and a processing pressure of 500 mTorr for 1 min, 3 min and 6 min. Next, two types of samples were subsequently treated with rapid thermal annealing (RTA) using a conventional thermal annealing system under ambient N₂ condition for 30 sec at a temperature of 600 °C. After that, the back-side contact of the Si wafer was deposited by Al film with a thickness of 300 nm. The sensing membrane size was defined through photolithographic processing under a photosensitive epoxy (SU8-2005, Micro-Chem). EIS structures were then fabricated on the copper lines of a printed circuit board (PCB) by using a silver gel to form conductive lines. Epoxy was utilized to separate the EIS structure and the copper line. The detailed EIS structure is illustrated in Fig. 1.

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Author Contributions
Chyuan-Haur Kao, Che-Wei Chang, Chan-Yu Lin, and Hsiang Chen designed the research. Che-Wei Chang graphed the device structure. Chia Lung Chang and Hsiang Chen devised the crystal growth method, grew and characterized the materials. Yu Tzu Chen, Wei Ming Su, Chien Cheng Lu analysed the data, and wrote the paper.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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