

Characteristics of a humidity sensor using a Na-doped hydroxyapatite thin film

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Abstract

A Na-doped hydroxyapatite (Na-HAp) thin film was prepared on a porous Al₂O₃ substrate using a pulsed laser deposition (PLD) technique. Crystallinity and composition were evaluated by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analysis. A humidity sensor was formed by establishing an inter-digital type Au electrode on the Na-HAp film. The humidity-impedance and humidity response of impedance characteristics were measured by an LCR meter. The results indicated that the Na-HAp thin film sensor showed excellent sensitivity and responsiveness to humidity conditions.

1. Introduction

Hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂; HAp] crystallized in a hexagonal structure (a=9.43Å, c=6.88Å) is the primary chemical constituent of bone and teeth and has been extensively evaluated for its biocompatibility; it has also been utilized in the medical field. Additionally, HAp has interesting chemical properties, such as adsorption and separation of proteins or nucleic acids and dehydration and dehydrogenation of alcohols, and thus may be employed as a chemical sensor or in electrochemical cells^(1, 2, 3). For applications in the medical and electrical industries, HAp thin films are required. Various deposition methods for preparation of HAp films have been reported, including radio frequency (RF) sputtering and ion-beam deposition^(4, 5). Recently, the pulsed laser deposition (PLD) method has been applied to produce pure crystalline HAp thin films^(6, 7, 8). Many reports on HAp thin films are related to dental and medical applications; however, few reports concern their electrical properties, as in our previous study⁽⁹⁾.

Herein, we describe the fabrication of Na-HAp thin films and their characteristics as humidity sensors. Na-HAp has significant advantages for humidity sensor applications for the following reasons: (1) Na-HAp is expected to exhibit improved electrical properties compared with normal HAp. HAp humidity sensors are very difficult to develop because HAp has a high resistivity at low humidity. (2) The electrical resistance of most ceramics tends to rise with irreversible adsorption of OH radicals, which increases with exposure to humidity, but since HAp contains OH radicals in its chemical makeup, it is less likely to be influenced by the presence of OH radicals.

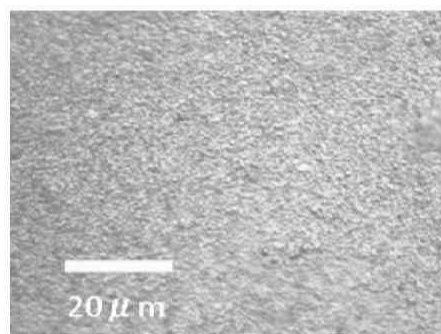


Fig. 1. SEM image of porous Al₂O₃ substrate.

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2. Experimental

To deposit Na-HAp thin films, the PLD technique using an ArF excimer laser ($\lambda=193$ nm) was employed. The laser was operated with a pulse duration of 20 ns at a repetition rate of 1~10 Hz during the experiments. The laser fluence on the target was approximately 1 J/cm². Na-HAp was prepared using pressed Ca₉Na(PO₄)₆(OH)₂ powder, which can be obtained from Na₂CO₃ and β -Ca₃(PO₄)₂ using typical solid-state reaction methods in an O₂+H₂O flow at 600 °C. Porous Al₂O₃ (10 mm×10 mm×1.0 mm *t*) was used as a substrate because it has a large surface area. Figure 1 shows a scanning electron microscope (SEM) image of the porous Al₂O₃. Graininess indicating the presence of many large islands is clearly seen; grains with a diameter of 100-150 nm and isotropic shape were characteristically observed at the surface of the porous Al₂O₃ substrate.

Prior to deposition, the vacuum chamber was evacuated to a background pressure of 3×10^{-7} Torr. The Na-HAp films were deposited under a gas pressure of 0.8 mTorr of pure O₂ +H₂O vapors at a substrate temperature of 100 °C. The typical deposition rate was 8 nm/min, and the total film thickness was about 300 nm. The as-deposited Na-HAp films were amorphous. Heat treatment after deposition was therefore carried out at 450 °C for 1 hr in an O₂+H₂O vapor atmosphere (10 ml/min). The films were then cooled to 100 °C for 1 hr under the same atmosphere.

The crystallinity of Na-HAp films was evaluated by X-ray diffraction (XRD) measurements, and film composition studies were conducted with a scanning electron microscope equipped with an energy dispersive X-ray analyzer (EDX). XRD patterns after annealing of Na-HAp films deposited on titanium and porous Al₂O₃ substrates are shown in Figure 2. The XRD patterns coincide with the standard pattern for HAp (JCPDS File Number 9-432) and show only peaks assigned to HAp and the substrate. Composition analysis by EDX determined the

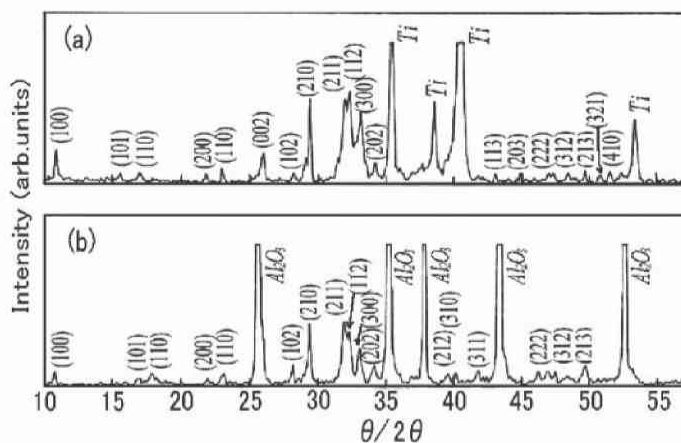


Fig. 2. X-ray diffraction pattern of Na-HAp films formed on (a) Ti and (b) Al₂O₃ substrates.

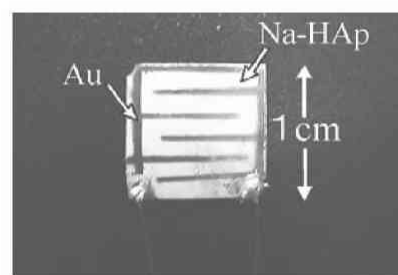


Fig. 3. Photograph of the humidity sensor using a Na-HAp film.

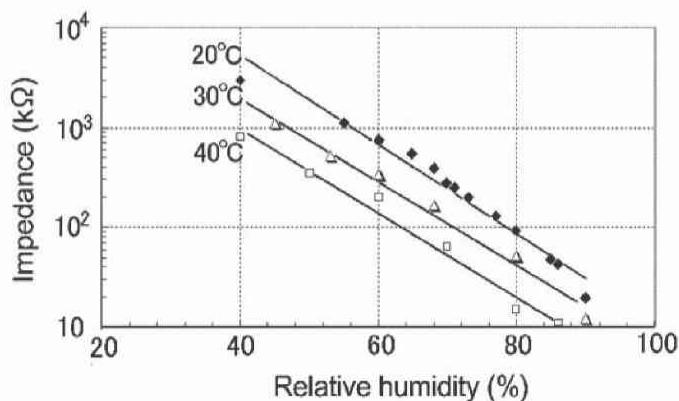


Fig. 4. Humidity-impedance characteristics of the humidity sensor using a Na-HAp thin film.

Ca/P ratio to be 2.02 and the Ca/Na ratio to be 9.04, indicating the presence of 0.96 mol% Na in the film.

3. Results and Discussion

The humidity sensor structure was formed by placing an inter-digital type Au electrode on the Na-HAp thin film (Figure 3). Humidity-impedance characteristics were measured using an LCR meter with an applied voltage of 1 V at 120 Hz. Impedance of the sensors was measured at relative humidities (RH) ranging from 40% to 90% in a constant temperature and humidity chamber. The results are shown in Figure 4. The logarithmic value of impedance decreased linearly with increasing humidity. Two orders of change in impedance were observed for this range of humidities. The sensor was then run through ten cycles of humidity changes from 40% to 90% RH to study its fatigue characteristics.

Next, the humidity-time response characteristics of the sensor were investigated. Figure 5 shows the results obtained at 40% and 80% RH. A high speed response for adsorption of about 10 sec and a desorption time of about 2 min were observed. The time-dependence for dry and wet cycles were both also found to be stable.

Various mechanisms to explain the correlation between resistance variation and humidity variation for the Na-HAp thin film sensor were considered. At the present time, we believe that the resistance variation is caused not by electronic transportation but by proton transportation via a mechanism similar to the one previously reported by J. H. Anderson⁽¹⁰⁾ and E. McCafferty⁽¹¹⁾ for electrical conduction by water absorption on the surface of metal oxide materials.

Our reasoning is based on the very high resistance ($>10^7 \Omega$) of the Na-HAp film (although with its carrier density of $10^{20} / \text{cm}^3$, it should be a good conductor). With such a high resistance, the fundamental transport mechanism should not be an electronic process, and thus humidity sensing cannot be based on an electronic transport mechanism. The fact that the surface of stoichiometric HAp shows good transportation for H_3O^+ ions strongly supports this notion.

We propose that Na substitution for the Ca enhances the H_3O^+ transportation on the surface. Substitution of divalent Ca by monovalent Na leaves a negatively charged chemical species and leads to formation of a vacancy in

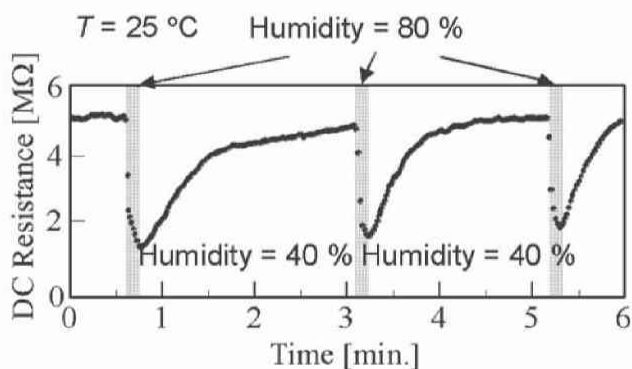


Fig. 5. Humidity-time response characteristics of the humidity sensor using a Na-HAp thin film.

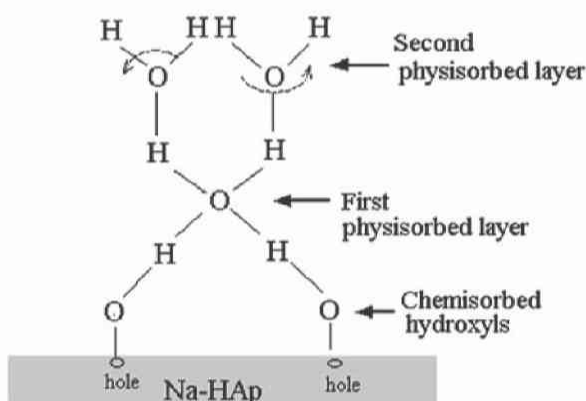


Fig. 6. Operational principles of the Na-HAp humidity sensor based on proton-type conductivity.

order to maintain charge neutrality, i.e., $(\text{Ca}_9\text{Na})(\text{PO}_{3.96\dots})(\text{OH})_2$ or $(\text{Ca}_9\text{Na})(\text{PO}_4)(\text{OH})_\delta$, where δ represents an OH vacancy. These kinds of vacancies will behave like holes and must show affinity with negatively charged species including the O atom in H_2O molecules, as shown in Figure 6.

Na substitution, therefore, enhances H_2O adsorption. Once H_2O molecules adsorb, the proton transport mechanism will be the same as that for HAp. H_2O molecules physisorb onto the surface of the Na-HAp film as a single molecular slab. In this situation, H_3O^+ is transported and hydrogen bonded onto the surface. Further physisorption of H_2O molecules in double layered H_2O molecular slabs occurs following transport of H_3O^+ , which is produced by the decomposition of the physisorbed H_2O molecules. The more physisorbed H_2O molecules there are, the more H_3O^+ ions exist to act as carriers. Therefore, higher humidity will cause a lower resistance in the Na-HAp film.

3. Conclusion

In conclusion, we have for the first time successfully prepared a crystalline Na-HAp thin film on a porous Al_2O_3 substrate using the PLD technique. A humidity sensor with an inter-digital Au electrode was fabricated using this thin film. The humidity-impedance and humidity response characteristics of the sensor were investigated and a large change of impedance and high response to humidity were observed. These results indicate that the Na-HAp thin film possesses favorable properties and may have application not only in humidity sensors but chemical sensors as well.

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和文抄録

Nd ドープハイドロキシアパタイト薄膜を用いた湿度センサの特性

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パルスレーザーデポジション (PLD) 法により、Nd ドープハイドロキシアパタイト (Na-HAp) 薄膜を多孔質 Al_2O_3 基板上に成膜した。薄膜の結晶性や組成は X 線回折 (XRD) およびエネルギー分散型蛍光 X 線分析 (EDX) によって評価した。Na-HAp 薄膜上にインターデジタル型の金電極を設けて、湿度センサとした。インピーダンスの湿度による変化と、湿度応答性を LCR メータにより測定した。その結果、薄膜センサは湿度に対して優れた感度と応答性を示した。

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