

Surface Passivation of the Thin-Film LAPS with Perhydropolysilazane-Derived Silica Treated by O₂ Plasma

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Here we describe a novel method for surface passivation of the thin-film light addressable potentiometric sensor (LAPS). In order to form a uniform passivation layer, perhydropolysilazane (PHPS) was utilized as a spin-coatable precursor of silica. After transformation of PHPS into silica by baking, we introduced an O₂ plasma treatment aiming for enhancement of the water resistance of the PHPS-derived silica (PDS) film by completing the PHPS-to-silica conversion. To confirm the effect of the O₂ plasma treatment, the PDS film was deposited on a thin-film LAPS electrode and tested by immersion in a cell culturing medium. The immersion test demonstrated that the plasma-treated PDS film could keep the electrode stable longer than the untreated could. With the treated PSD film of 600 nm in thickness, a lifetime of the thin-film LAPS was estimated at over two weeks, which is sufficient for cell culturing experiments.

Keywords : perhydropolysilazane, silica, LAPS, passivation, O₂ plasma treatment

1. Introduction

In order to improve the spatial resolution of the light addressable potentiometric sensor (LAPS), amorphous silicon (a-Si) has been utilized as a thin-film photoconductor instead of bulk Si⁽¹⁾. Due to the vulnerability of a-Si to alkaline, the thin-film LAPS requires surface passivation for long-term use in biological electrolytes like cell culturing media, pH of which most often ranges between 7.2 and 7.6. Although our previous works have proposed a conductive passivation layer⁽²⁾⁻⁽⁴⁾, few studies investigated insulating materials for a stable electrolyte-insulator-semiconductor (EIS) interface on the thin-film LAPS.

Recently, perhydropolysilazane (PHPS), which is an inorganic polymer with Si-N skeleton, has drawn attention as a liquid precursor of SiO₂⁽⁵⁾. Because of the easy fabrication process, spin-coat and bake, the PHPS-derived silica (PDS) coating could be an attractive option for surface passivation of the thin-film LAPS. To our knowledge, however, little is known on how stable the PDS film is in the biological environment.

Here in this study we investigated the water resistance property of the PDS film by a long-term immersion test in a cell culturing medium. Previous studies on PDS have pointed out that the extent of PHPS-to-silica conversion is a critical factor for the film stability^{(5),(6)}. In order to enhance the water resistance of the PDS film, therefore, we introduced and evaluated an O₂ plasma treatment, which is expected to remove nitride residues and other impurities at the PDS surface⁽⁷⁾.

2. Materials and Methods

The thin-film LAPS electrodes were fabricated with the PDS passivation coating. During the immersion test, dark impedances and luminous sensitivities (dark to bright impedance ratios) of the electrodes were monitored to detect the deterioration of PDS and a-Si⁽²⁾. The different test conditions are summarized in Table 1.

A PHPS solution in xylene (20 wt% with catalysts for low-temperature transformation; Clariant, NL110A) was spin-coated on an SnO₂ conductive glass substrate (AGC Fabritech, A110U80), on which hydrogenated amorphous silicon (a-Si:H) had been deposited by chemical vapor deposition. After baking at 250 °C for 2 h, the substrate was treated with O₂ plasma at 150 W for 5 min in a vacuumed reactor (Yamato, PR31). The SnO₂ layer was, then, partly exposed by wet etching of the a-Si:H layer to be wired to external devices. Lastly, a plastic dish with a Φ-4mm through hole on bottom was attached as a solution chamber.

In the immersion test, the electrodes were exposed to Dulbecco's Modified Eagle Medium (DMEM) in a humidified incubator at 37 °C with or without 5 % CO₂, which makes pH of DMEM 7.2 or >9, respectively. The test condition with pH of >9 was used to accelerate electrode deterioration due to alkaline. During the immersion, dark and bright impedances at 1 kHz were intermittently measured with the LCR meter (Agilent

Table 1. Summary of the test conditions.

Electrode #	Film thickness (nm)		Plasma treatment	pH
	a-Si:H	PDS		
1	1000	-	-	>9
2	1000	600	Untreated	>9
3	1000	600	Treated	>9
4	1000	600	Treated	7.2
5	140	300	Treated	7.2

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Technologies, 4274A) in dark and under illumination, respectively. For light illumination, a 150-W halogen lamp was utilized.

3. Results and Discussion

Figure 1 shows time courses of the dark impedances and luminous sensitivities of different substrates. Both the no-coated electrode (electrode #1) and the electrode with an untreated PDS layer (#2) exhibited decreases in the dark impedance and luminous sensitivity, while those of the electrode with the O₂ plasma-treated PDS layer (#3) reached stable plateau. The decrease of the luminous sensitivity accompanied with the decrease of the dark impedance means water penetration to the a-Si:H layer and its subsequent dissolution. The initial decrease and increase observed in the dark impedance and luminous sensitivity of the electrode #3 seem to reflect surface hydration of the PDS film not deterioration, because the same phenomenon was observed in an immersion test with a neutral saline solution instead of DMEM (data not shown). These observations clearly demonstrate that the O₂ plasma treatment can enhance the water resistance of the PDS film. Then, the stable duration of the thin-film LAPS electrode was estimated in the standard biological condition, i.e. in DMEM of pH 7.2 with 5% CO₂. Both the test electrodes with the O₂ plasma-treated PDS layer (#4) and with the thinner a-Si:H and PDS layers (#5) showed stable time courses of the impedances over two weeks. This long-term stability will be sufficient for biological experiments even including cell culturing.

The previous studies on PDS reported that the stability of the

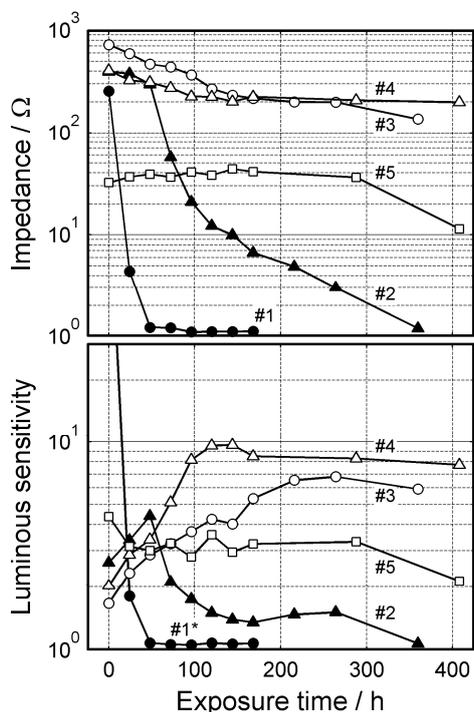
PDS film increases as the PHPS-to-silica conversion proceeds^{(5),(6)}. The O₂ plasma treatment was reported to effectively purify the skeletal network of sol-gel-derived SiO₂⁽⁷⁾, and thus is expected to complete the PHPS-to-silica conversion. The water resistance enhancement of the PDS film by the O₂ plasma treatment, therefore, is well consistent with these studies.

Regarding a cell-semiconductor hybrid on the conventional LAPS, SiO₂ was found to be a more effective insulating material than Si₃N₄⁽⁸⁾, which has been the first choice for the EIS configuration⁽⁹⁾. With the PDS film shown here, the concept of on-LAPS cell monitoring can be expanded to the thin-film LAPS, although some effort would be necessary to make the PDS layer thinner for the more efficient capacitive coupling between a-Si and cells.

4. Conclusion

The main findings of this study were that the O₂ plasma treatment enhances the water resistance of the PDS film, and that the plasma-treated PDS film can protect the thin-film LAPS electrode from corrosion in the biological electrolyte. The immersion test in DMEM with impedance monitoring confirmed an over two-week lifetime of the thin-film LAPS electrode with the plasma-treated PDS passivation layer, while the electrode with the untreated immediately deteriorated. With this long-term durability, this simple and reliable method of surface passivation will be applicable for the cell-semiconductor hybrid on the thin-film LAPS.

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Time courses of the measured dark impedances (top panel) and luminous sensitivities (bottom). Each line corresponds to the coating and test condition indicated and numbered in Table 1. *: The luminous sensitivity value of the electrode #1 at 0 h was about 200 and out of the range shown.

Fig. 1. Time courses of the electrode impedances during the immersion test.

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