Versatile surface functionalization of inorganic materials with cyclic phosphoesters

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Introduction: The use of reactive alkoxysilanes and chlorosilanes to modify the surface properties of inorganic materials is a process that is widely used in both research and technology. However, these silanes are sensitive to moisture and require specific reaction conditions. Furthermore, unfavorable byproducts are also generated through the reaction of chlorosilanes with metal oxide surface. In the current study, we have firstly founded that the cyclic phosphoester (CP) compounds are useful for surface modification of inorganic materials.

Methods: Si wafers were purchased from Yamanaka Semiconductor Co., Ltd., Tokyo, Japan. 2-Ethoxy-2-oxo-1,3,2-dioxaphospholane (EP), 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane (IP), and 2-(2-oxo-1,3,2-dioxaphosphoroyloxyethyl-2-bromoisobutylate) (OPBB) were synthesized by condensation reaction.[1,2] CP compounds were spin coated on cleaned Si wafers from their ethanol solutions and the wafers were annealed at 100°C for given periods.

Spectroscopic surface analyses were performed by X-ray photoelectron spectroscopy (XPS) and FT-infrared reflection absorption spectroscopy (FTIR-RAS). Advancing (θ_A) and receding (θ_R) water contact angle was measured with addition to and withdraw from the drop, respectively. The morphology of sample surfaces treated with CP compounds was observed with atomic force microscope (AFM).

To better understand biointerfacial advantages of modified surfaces, well-defined polymer brushes consisting of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) were prepared by atom transfer radical polymerization (ATRP) through an OPBB monolayer. The protein adsorption on sample surfaces was determined by microscopic observation after contact with 4.5 g/L fluorescence labeled-albumin for 30 min at 37 °C.

Results: Figure 1 shows water contact angle data for Si wafers modified with EP and OPBB. As a result of water contact angle measurement, the surface modified with CP compounds was more hydrophobic than unmodified Si wafer surface (θ_A/θ_R=26°/10°). The water contact angle of CP-immobilized surfaces increased with annealing at 100°C and reached plateau after 10 min-anneal. Moreover, the contact angle data for OPBB-immobilized surfaces was significantly higher than that of EP-immobilized surface at the plateau region. From FTIR-RAS analysis, absorption at 680 cm^{-1} due to Si-O-P was observed for CP-immobilized surfaces and the signal became remarkable with increasing in the annealing period. AFM images for CP-immobilized Si wafer indicated sub-nano level and a very smooth layer of CP compounds was formed on Si wafer surfaces. XPS P_{2p} signal was attributed on OPBB-immobilized Si wafer.

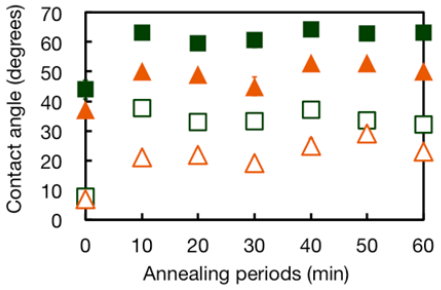

Figure 1 Water contact angle data for OPBB- and EP-immobilized silicon wafer surfaces.
■:θ_A (OPBB); □:θ_R (OPBB); ▲:θ_A (EP); △:θ_R (EP).

Generation of PMPC brushes on OPBB-immobilized Si wafer *via* ATRP was confirmed by XPS and FTIR-RAS analyses. We also succeeded to fabricate micropatterns of the PMPC brushes by the selective decomposition of the OPBB monolayer with UV light-irradiation.[3] The distribution of PMPC brushes was also confirmed by AFM observation. Figure 2 shows fluorescence micrograph of micropatterned PMPC brush surface in contact with fluorescence labeled albumin. On the UV-irradiated region that has no polymer brush; the fluorescence intensity was significantly high, indicating that a large amount of BSA is adsorbed in this region. Conversely, BSA adsorption was remarkably reduced in the PMPC polymer brush layer.

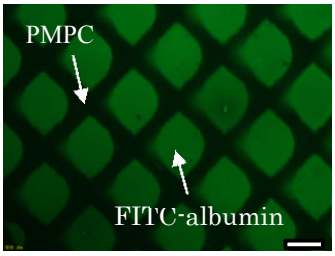

Figure 2 A fluorescence micrograph of FITC-albumin adsorption on PMPC brush patterned surface after contact with 4.5mg/ml FITC-albumin in PBS for 30min. Bar is 50μm.

Conclusions: CP compounds worked as surface modification reagents for inorganic materials. Versatile surface modification can be performed with CP compounds because they are obtained from the condensation of alcohol and cyclic chlorophosphate.

References: 1) Iwasaki Y. et al., *Macromolecules* **2004**;37:7637. 2) Iwasaki Y. et al., *Macromolecules* **2010**;43:2664. 3) Iwata R. et al., *Biomacromolecules* **2004**;5:2308.

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