Sensors and Actuators B 270 (2018) 97–103

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Gas-sorption properties and structures of carbonaceous films prepared by radio-frequency sputtering of Japanese calligraphy solidink disc

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ARTICLE INFO

Article history:
Received 5 August 2017
Received in revised form 17 March 2018
Accepted 26 April 2018
Available online 27 April 2018

Keywords:
Quartz crystal resonator
Radio-frequency sputtering
Carbonaceous film
Polypeptide
Linear solvation energy relationships

ABSTRACT

Japanese calligraphy solidink (sumi) is essentially made of dried gelatinous carbon and collagen peptides composed of enzyme-catalyzed gelatin. Humin-like carbonaceous films with packed columnar structures were prepared by the radio-frequency (rf) sputtering of these gelatin-based polypeptides. The collagen film has a slightly-cleft structure, whereas the sumi film has remarkably developed clefts. The sumi film has a lower elemental ratio of nitrogen than the collagen film. The well-cleft and nitrogen-poor characteristics of the sumi film are considered to be due to the oxidative species generated by the rf discharge of water vaporized from the sumi disc sputtering target. Collagen films have high absorption capacities for small polar species such as water, methanol, and ethanol. This selectivity is attributable to the densely packed columnar structure with electronegative atoms such as nitrogen and oxygen inducing high affinity for polar species. Linear solvation energy relationships were used to model the absorption behaviors of these carbonaceous films by means of the polar and dielectric characteristics of absorbate molecules. These physicochemical molecular descriptors are distinguishing attributes for the gas-sorption of carbonaceous sputtered films of gelatin-based polypeptides.

1. Introduction

Similar to the biological decomposition of biomaterials, biomaterials are carbonized by electrical discharge. We previously reported the preparation of carbonaceous gas-adsorptive films by the radio-frequency (rf) sputtering of amino acids [1] and a polysaccharide pectin [2]. In this study, we investigate the preparation of carbonaceous gas-sorption films by the rf sputtering of collagen-based biopolymers. Collagen-based polypeptides represented by gelatin are used in industries such as medicine, cosmetics, and ingredients, as well as in artisanal crafts as a natural glue. The rf sputtering of polypeptides for preparing gas-sorption films has never been reported, to the best of our knowledge.

We considered the Japanese calligraphy solidink (sumi), which is a novel carbonaceous film raw material for use as a gas-sorption layer, as a sputtering target. Sumi is composed of gelatin and lampblack soot (carbon powders), and the typical weight ratio of gelatin to lampblack soot is ~0.6 [3]. Lampblack soot generally consists of spherical carbon particles with diameters of several tens of nm [4,5]. Gelatin consists of collagen polypeptides, which are subject to carbonization by rf-sputtering, whereas carbon cannot be easily sputtered to build up deposits owing to its low sputtering yield [6]. Gelatinous carbon particulates contain residual water (called combined water) even after intensive drying processes are carried out. The residual water and carbon particulates potentially affect the sputtering processes for producing gelatin-origin carbonaceous films.

Sumi is a promising and novel sputtering target for preparing carbonaceous films. Deposition is carried out under the discharge of a sputtering gas in which water is slightly added from the sumi target. According to the traditional manufacturing process, soot particles are uniformly mixed with gelatin paste forming a clayey dough by repeated kneading and pounding. The clayey dough is subsequently molded and dried gradually over several months in dry air to prevent cracking. The content of residual water in sumi depends on the drying condition and on the colloidal activity of gelatin, which is likely to deteriorate with aging. The residual water in sumi is not easily removed completely even after long-term evacuation in combination with heating. Therefore, the rf sputtering of sumi is conducted in an oxidative condition in which reactive oxidants such as hydroxyl radical and singlet oxygen are generated by the rf discharge of water supplied from the sumi target.

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https://doi.org/10.1016/j.snb.2018.04.153
0925-4005/

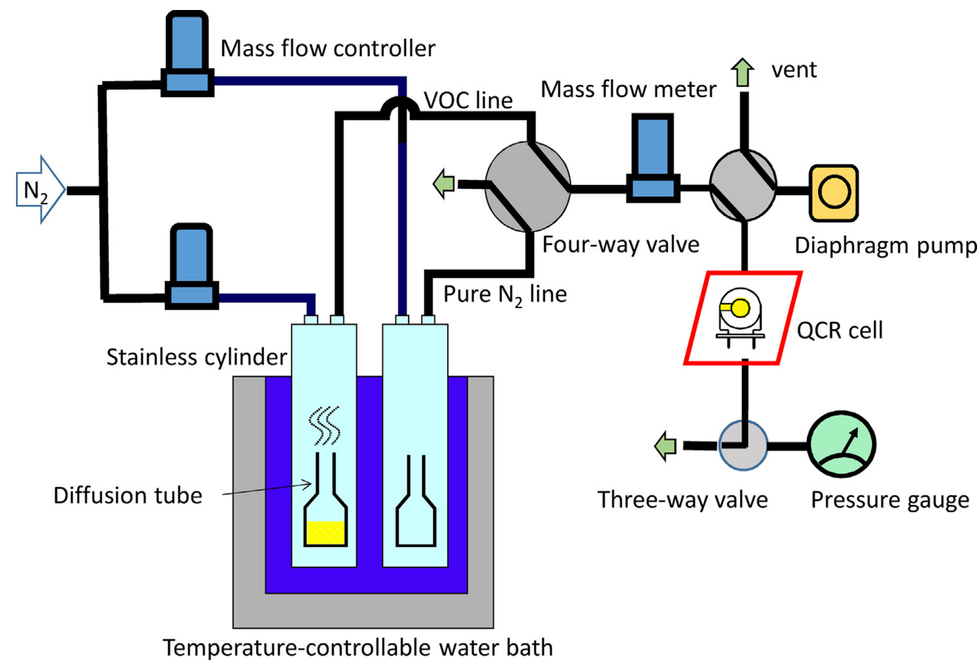

Fig. 1. Schematic of the equipment used to measure the gas-sorption characteristics of the QCR sensors.

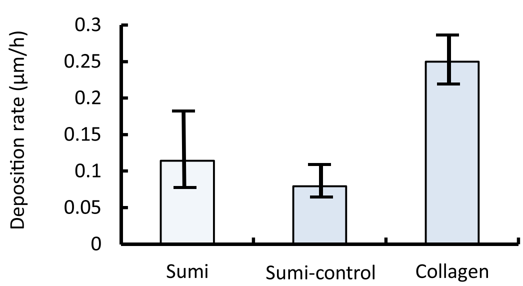

Fig. 2. Deposition rates of carbonaceous sputtered films during rf sputtering of the gelatin-based polymers.

The carbonization of gelatin by rf sputtering is expected to prepare gas-sorptive carbonaceous films. This oxidative effect of the water-contaminated plasma gas may be enhanced by the conductive lampblack soot, which potentially plays the role of a latent heat storage material.

In this paper, we report the columnar structures and gas-sorption characteristics of the carbonaceous films prepared by rf sputtering of sumi and its major components (collagen polypeptides and carbon). It is intriguing whether sumi could be used as a sputtering target to prepare carbonaceous films appropriate for gas sensing.

The structure and gas-sorption performance of the sumi-sputtered films were verified by comparing them with sputtered films of collagen, which is the main component of gelatin. We used the enzyme-catalyzed collagen polypeptides instead of gelatin, which may contain many kinds of contaminants. In addition to collagen polypeptides, we used the sumi-control, which was prepared by mixing carbon powder with collagen polypeptides at the identical ratio traditionally used in the manufacture of sumi. This study compares the structure and gas-sorption characteristics of sumi-sputtered films with that of sputtered films of collagen polypeptides.

2. Experimental

The sumi disc was manufactured by Kobaien Corp. (Nara, Japan) according to the traditional process. According to the artisanal manufacturing procedure, the soot from flaming vegetable rapeseed oil produces carbon powder, which was uniformly mixed with gelatin paste. A mixture of carbon and gelatin was molded to a clayey dough by repetitive kneading and pounding. The clayey dough was shaped to 150 mm in diameter and 10 mm in thickness, and gradually air-dried over a month via dusting in dry ash to prevent cracking.

The sumi disc was set concentrically on a polyethylene (PE) disc (170 mm in diameter, 10 mm thick), which was placed on the base electrode connecting the 13.56 MHz rf power supply in a diode-type rf sputtering apparatus with sputter-up configuration (see Fig. S1). Polished Si wafer chips and 9 MHz AT-cut quartz crystal resonators (QCRs) with gold electrodes were used as the sputtered film substrates, installed on the water-cooled upper grounded electrode.

The residual water in the sumi disc is likely to vaporize in high vacuum processes. After two days' evacuation using a 250 L s^{-1} turbomolecular pump, the pressure of the 7 L chamber equilibrated at 6×10^{-3} Pa in combination with heating of the chamber to 340 K. Ar was introduced into the chamber at 20 mL min^{-1} during evacuation by a 150 L min^{-1} mechanical booster pump. The chamber pressure was kept constant at 7 Pa by controlling the conductance valve. Rf power was applied at 110 W (corresponding to 0.48 W cm^{-2}) and the substrate temperature was kept at 293 K during sputtering deposition. Long-term sputtering was conducted repeatedly without breaking the vacuum. One side of the QCR was deposited with carbonaceous film to a thickness of about 1.8 μm. The film-coated silicon chips used for structural analyses were stored in pure N_2 to prevent contamination and oxidative aging.

The sputtering target of collagen polypeptides was prepared according to the method reported previously [1,2]. The weight ratios of collagen to carbon were 0.6 and 0 (carbon free), which are called "sumi-control" and "collagen", respectively. The collagen polypeptide with a mean molecular weight of 2000 Da and amorphous carbon powder (99.999%, ~325 mesh) with a density of 1.8–2.1 g cm^{-3} were purchased from Wako Chemical Co. and used without further purification. Collagen polypeptide was obtained