Adsorption properties of polymer thin films prepared by r.f. sputtering with a BPDA-PDA polyimide target

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1. Introduction

Polyimide (PI) has excellent thermal stability, chemical stability and mechanical properties. PIs are often used as insulators in flexible print circuit boards, aerospace materials, tribological materials and other function materials. PI thin films have also some excellent properties. Kitoh et al. [1] reported tribological properties of sputtered thin films with a PI target in various sputtering condition and the sputtered thin films with a PI target have excellent tribological properties. We had already reported that molecular structures of target materials effected on elemental compositions, tribological properties and pull strengths between thin films and copper substrates [2,3]. Choukourov et al. [4] reported that sputtering conditions affected on elemental compositions and chemical bonding states of PI sputtered thin films. Further, we had already reported that sputtered thin films with nitrogen gas had good wear durability [3,5].

In this study, we focus on a surface property of these thin films prepared by an r.f. sputtering with a polyimide. Especially, we report on a gas adsorption property of the thin films deposited onto the QCM by an r.f. sputtering systems.

2. Gas adsorption properties of sputtered thin films prepared with a PI target

Deposition of polymer thin films by an r.f. sputtering

An r.f. sputtering apparatus equipped with a PI target was used for the thin film coatings. Figure 1 shows molecular structure of the PI target used in this study.



Fig.1 Molecular structure of the BPDA (Biphenyl dianhydride)-PDA(para phenylene diamine)

We'd already reported that elemental compositions and chemical bonding states of these thin films were changed

by pressure and r.f. power during sputtering, which affected on the adhesion strength and shear stress of the thin films [6]. In this study, we prepared these sputtered thin films at 150W-0.6Pa, 150W-3.0Pa and 25W-3.0Pa. Coating thickness of the thin films on the gold electrode of QCM was 30 nm.

Measuring system of gas adsorption

Adsorption properties of these thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were evaluated by measuring frequency shifts using the QCM system. Fig.2 shows molecular structures of these volatile organic compounds.



Fig.2 Molecular structures of volatile organic compounds



Fig.3 Schematic diagram of adsorption gas measuring system with QCM

After a liquid of these volatile organic compounds was dropped into gas washing bottle, dry nitrogen was flown into the gas washing bottle at 300mL/min. The volume of each liquid used was 500μ L. Change in QCM oscillating mass due to gas adsorption to the gold electrode of QCM was indicated as the frequency shifts. Fig.3 shows a schematic diagram of adsorption gas measuring system with QCM. The QCM system was maintained at 20 ± 1

Change in the frequency was plotted as a frequency shift per μ g polymer thin film. Adsorption properties of these polymer thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were evaluated. Change in QCM oscillating mass, Δm , can be calculated by the Sauerbrey's equation as follows [7];

$$\Delta f = -\frac{\Delta m \times F^2}{N \times S \times r}$$
(1)

 $\Delta m = 0.69 \times \Delta f$ [ng]

where f is change in frequency, m is change in the QCM oscillating mass, F is fundamental frequency of QCM, N is frequency constant (AT-cut is 167 cm \cdot kHz), S is surface area and r is density of the crystal (2.65g/cm³). In this study, relationship between m and Δf can be represented as following:

(2)



Fig.4 Changes in frequency due to gas adsorption to the sputtered thin films deposited onto the gold electrode of QCM

Adsorption masses of these gases except for toluene in the sputtered thin film prepared at 25W-3.0Pa were highest among those in the three thin films. We'd already analyzed chemical structures of these thin films by FT-IR. We could not see clear peaks which represented functional groups in the sputtered thin films prepared at 150W-0.6Pa and 150W-3.0Pa. However, we could see only a few peaks which would represent functional groups in the sputtered thin films prepared at 25W-0.6Pa [6].

In addition, water contact angle on the sputtered thin films prepared at 25W-3.0Pa was highest of all the three thin films. These volatile organic compounds except for toluene are polar solvents. The water contact angles decreased with increase of adsorption masses of volatile organic compounds except for toluene. On the contrary, the water contact angles increased with increase of adsorption mass of toluene. The adsorption masses of these volatile organic compounds seem to relate with the water contact angles on these thin films.

3. Conclusions

Thin films were deposited by an r.f.sputtering with a BPDA (Biphenyl dianhydride)-PDA(para phenylene diamine) target on gold electrode of QCM. Adsorption properties of these thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were evaluated. Chemical structures, especially wettabilities of surface of the thin films would effect on the gas adsorption properties.

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