P-10-20

Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp655-656

Gas adsorption properties of fluorocarbon polymer thin films prepared by three different types of r.f. magnetron sputtering systems

Norihiko Hasegawa [1], Satoshi Yano [1], Satoru Iwamori [1] and Kazutoshi Noda [2]

[1] Kanazawa University, Graduate School of Natural Science & Technology
Kakumamachi, Kanazawa, Ishikawa 920-1167, Japan
Phone: +81-76-234-4950 E-mail: iwamori@t.kanazawa-u.ac.jp
[2] National Institute of Advanced Industrial Science and Technology (AIST)
16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

1. Introduction

Poly(tetrafluoroethylene) (PTFE) has been widely used in various industries. The PTFE thin films can be coated by various methods, i.e. sol-gel method, chemical vapor deposition (CVD) and physical vapor deposition (PVD). There are a lot of reports on the PTFE thin films prepared by PVD methods, such as vacuum evaporation and r.f. sputtering. Many researchers had reported on properties of the fluorocarbon polymer thin films prepared by r.f. sputtering or r.f. magnetron sputtering with a poly(tetrafluoroethylene) target [1-4]. For examples, surface morphologies and chemical structures of these fluorocarbon polymer thin films were already reported. In addition, mechanical and tribological properties of these fluorocarbon polymer thin films were also reported [3, 4]. We've already reported on an effect of magnetic fields in an r.f. sputtering system on these properties [5]. Surface morphology and chemical structure of the thin film prepared by magnetron sputtering equipped with strong magnetic field were different from those by magnetron sputtering equipped with weak magnetic field. The fluorocarbon thin film prepared by unbalanced magnetron sputtering had the middle characteristic between those of the thin films prepared by the strong and weak magnetron sputtering systems.

In addition, highly sensitive detection technologies for volatile organic compounds are needed. Quartz crystal microbalance (QCM) method is one of effective methods for detection. In this paper, we report on gas adsorption properties of these fluorocarbon polymer thin films deposited onto the QCM by three types of r.f. magnetron sputtering systems with a strong, a weak and an unbalanced magnetic fields.

2. Gas adsorption properties of fluorocarbon polymer thin films

R.f. magunetron sputtering

An r.f. sputtering apparatus equipped with a magnetic field beneath the PTFE target was used for the fluorocarbon polymer coatings. Figure1 shows a schematic diagram of magnetron sputtering system, and magnetic fields used in this experiment are summarized in Table1. The PTFE target and substrates are equipped onto down and upper electrodes respectively. Distance between the upper electrode and top surface of the PTFE target was 40mm.

Measuring system of gas adsorption

Coating mass of these polymer thin films on the gold electrode of QCM were determined by the QCM system. The coating mass of these polymer thin films was 1.3-1.8μg. 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.

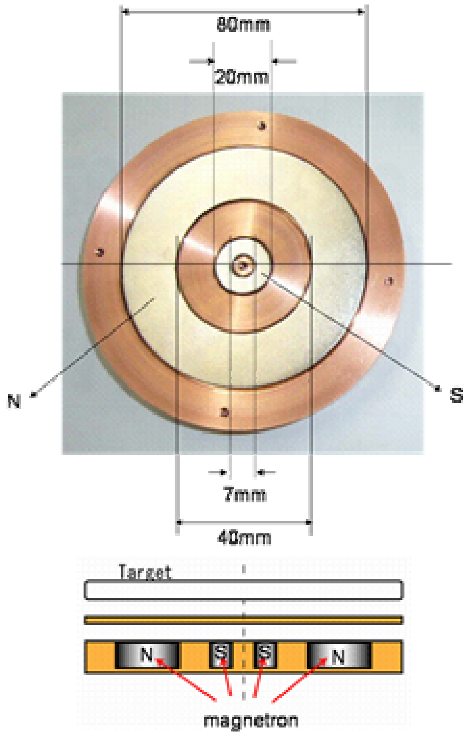

Fig.1 Schematic diagram of magnetron sputtering systems

After a liquid 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 500μL. Change in QCM oscillating mass due to gas adsorption to the gold electrode of QCM was indicated as the frequency shifts. The QCM system was maintained at 20±1 ℃.

Fig. 2 shows changes in frequency due to gas adsorption to these polymer thin films deposited onto the gold electrode of QCM. Change in the frequency was plotted as a frequency shift per μg 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 [6];

Table I Magnetic fields in magnetron sputtering systems

	N	S
Strong	3600	3600
Weak	1000	1000
Unbalanced	3600	1000

(Gauss)

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

where Δf is change in frequency, Δm is change in the QCM oscillating mass, F is fundamental frequency of QCM, N is frequency constant (AT-cut is 167 cm・kHz), S is surface area and r is density of the crystal (2.65g/cm^3). In this study, relationship between Δm and Δf can be represented as following:

$$\Delta m = 0.69 \times \Delta f \quad [\mathrm{ng}] \qquad (2)$$

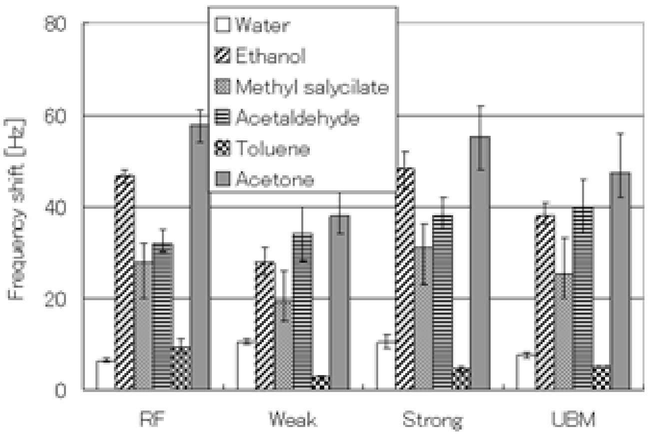

Fig.2 Changes in frequency due to gas adsorption to polymer thin films deposited onto the gold electrode of QCM

Adsorption mass of toluene was lowest of all volatile organic compound gases. These volatile organic compounds except for toluene are polar solvents. These polymer thin films have low sensitivities to non-polar solvents which contain methyl and aromatic groups, and high sensitivities to polar solvents which contain carbonyl and hydroxyl groups. In particular, methyl salicylate contains benzene ring as well as toluene, however a carbonyl and hydroxyl groups are also contained in the molecule. The carbonyl and hydroxyl groups would effect on larger adsorption mass compared to that of toluene in these polymer thin films.

Adsorption mass of these volatile organic compounds slightly increased with increase of magnetic fields. We'd already reported that surface morphologies and chemical structures of these fluorocarbon polymer thin films [5]. Chemical structures of these polymer thin films were different. Elemental ratio, F/C, of these fluorocarbon thin films prepared by these magnetron sputtering systems decreased with increase of magnetic fields. In addition, many tiny prominences, whose diameter and height were 10–30 nm in base and several nm in height, can be observed at the surface of the thin film deposited by magnetron sputtering with the strong magnetic field. However, larger prominences, whose diameter and height were several hundreds nm in base and several nm in height, can be observed at the surface of the thin film deposited by the magnetron sputtering with weak magnetic field [5].

The surface morphologies and chemical structures of these fluorocarbon polymer thin films may effect on these gas adsorption properties.

3. Conclusions

Fluorocarbon polymer thin films were deposited with a poly(tetrafluoroethylene) target by three different types of r.f. magnetron sputtering systems with strong, weak and unbalanced magnetic fields. Adsorption properties of these thin films for water, ethanol, acetone, acetaldehyde, toluene and methyl salicylate were evaluated. Chemical structures and surface morphologies of these polymer thin films would effect on the gas adsorption properties.

Acknowledgements

This work was partially supported by Grant-in-Aids for the Scientific Research C (21560744) from the Japanese Ministry of Education, Culture, Sports, Science and Technology.

References

[1] Y.Yamada and T.Kurobe, Jpn. J. Appl. Phys., **32** (1993) 5090.
[2] H. Biederman, Vacuum, **59** (2000) 594.
[3] Y.Nagayama, S.Iwamori and Y.Yamada, J. Vac. Soc. Jpn., **46**(2003) 827.
[4] S.Iwamori, K.Keduka and A.Uemura, J. Soc. Mater. Sci. Jpn., **57**(2008)611.
[5] J S. Iwamori, N. Hasegawa and A. Uemura, Surface and Coatings Technology, **203**(2008)59.
[6] G. Sauerbrey and Z.Phys., **155** (1959)206