B-5-5L
Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp686-687

Antireflective Protective Coating by Ion-Assisted Vapor Deposition Polymerization of Fluoropolymer Thin Films

Kazuo Senda[1, 2], Tsuyoshi Matsuda[2], Kuniaki Tanaka[2], and Hiroaki Usui[2]

[1] Sumitomo Precision Products Co., Ltd.
Fuso-cho, Amagasaki, Hyogo, 660-0891, Japan
Phone: +81-6-6482-8811 E-mail: senda-k@cc9.ne.jp
[2] Tokyo Univ. Agricul. & Technol.
Naka-cho, Koganei, Tokyo 184-8588, Japan

1. Introduction

Due to the recent advancement of mobile electronic devices, display panels are frequently operated in the outdoor environment. In addition, requirement for touch-panels is rapidly increasing. In these circumstances, there is a strong demand for protective and antireflective coating for the display panels. The conventional antireflective coating consists of multilayer of inorganic thin films. However, future flexible displays require flexible coatings that would not crack like the oxide antireflective coatings. This paper proposes to use a vapor-deposited fluoropolymer thin film for the flexible, antireflective, and inert surface coatings.

The fluoropolymers have unique characteristics such as low refractive index, high transparency, chemical and thermal stability, low surface energy, etc. In this work, fluoropolymer thin films were prepared by vapor deposition of monomers under ion irradiation, i. e. ion-assisted deposition (IAD). This technique enables to form polymer thin films directly from their monomers without using organic solvents. The ion irradiation not only induces the polymerization reaction but also improves the interface characteristics between the film and the substrate. The adhesion strength of the IAD film was compared with a typical fluoropolymer film prepared by the spin-coating.

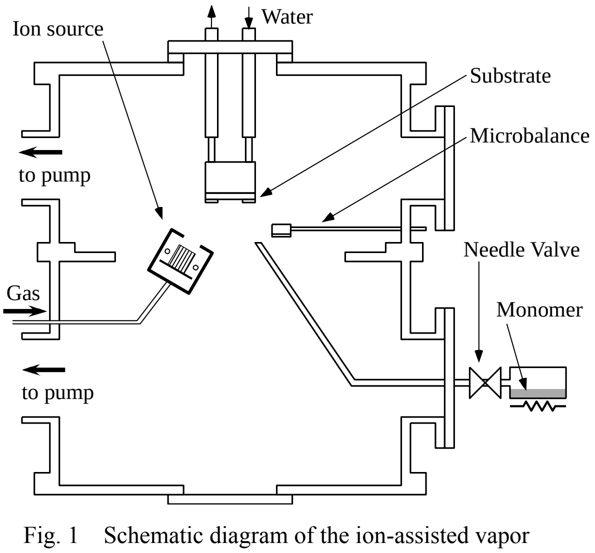

Fig. 1 Schematic diagram of the ion-assisted vapor deposition polymerization apparatus.

2. Experimental

Figure 1 shows the schematic diagram of the IAD apparatus. The monomer for film formation, 2-(perfluorohexyl) ethylacrylate (Rf-6), was evaporated and introduced into the high-vacuum chamber through a needle valve and deposited on the glass substrate that was cooled to -10^{o}C. At the same time, the substrate was irradiated with argon ions generated by an electron bombardment type ion source. The ion current was about 0.5 μA/cm^2, and the typical ion energy was 100 eV. Formation of fluoropolymer was confirmed by infrared (IR) spectroscopy. For comparison, films were also prepared by spin-coating Teflon AF1600 (DuPont) from its solution in dichloropentafluoro propane (HCFC225). The adhesion strength of these films was examined by the tape test (JIS K 5400-8.5) and also by ultrasonic agitation in water and HCFC225. Optical reflectivity of the film was measured with a spectrophotometer.

3. Results and Discussion

Formation of Fluoropolymer Thin Films

The Rf-6 monomer has low sticking probability to the substrate surface, and no films were obtained by simply depositing its vapor without the ion irradiation. On the contrary, uniform films were obtained when the Rf-6 was deposited under the irradiation by Ar ion beam of 50 to

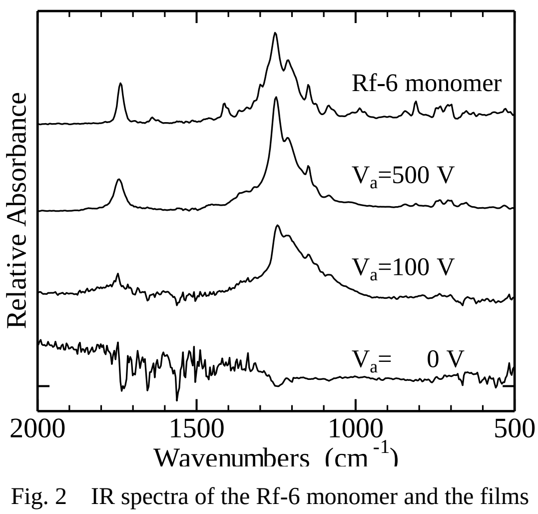

Fig. 2 IR spectra of the Rf-6 monomer and the films deposited at ion energy V_a of 0, 100 and 500 eV.

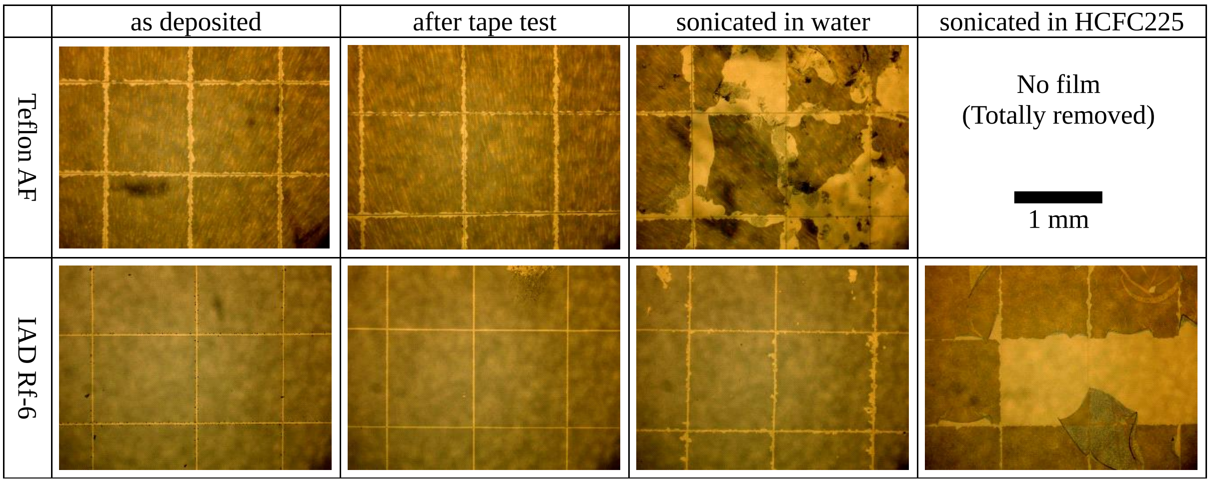

Fig. 3 Optical microscope images of spin-coated Teflon AF (upper) and IAD-Rf-6 (lower) films in the as-deposited state, after tape test, and after sonication in water and HCFC225.

1000 eV. The formation of fluoropolymer was confirmed by the IR spectra as shown in Fig. 2, indicating the C-F vibration bands in 1100 to 1300 cm^{-1} and disappearance of the vinyl band. It was found that the film thickness increases with increasing ion energy due to the enhancement of polymerization reaction. However, irradiation by high energy ions tended to modify the film characteristics. At the ion energy of 100 eV, the surface free energy of the film was 10.3 mJ/m, which is a typical value for fluoropolymers. However, the surface energy increased to 19.0 mJ/m by increasing the ion energy to 1000 eV. The ion energy was set to 100 eV hereafter.

Adhesion Strength

The Rf-6 film deposited by IAD and a spin-coated film of Teflon AF1600 were cross-cut into 1 mm square by a razor blade, and were tested by the JIS standard tape test, and then by sonicating in water and HCFC225 successively. Figure 3 shows the optical microscope images after these adhesion tests. The adhesive tape did not stick to these films due to the low surface energy, and no damage was observed by the tape test. By sonicating in water, the IAD film was barely damaged, but the spin-coated film partly detached from the substrate. By further sonicating in HCFC225, the IAD film started to came off, while the spin-coated film was totally removed. These results indicate that the IAD film has higher adhesion strength to the substrate compared to the spin-coated film. This result reflects the well-known fact that the ion irradiation is effective to improve the film-substrate interface [1].

Antireflective Characteristics

Fluoropolymer is unique in its low refractive index, and can be utilized as a single-layer antireflective coating. The refractive index of Rf-6 monomer is 1.336, and its deposited film is expected to be effective for this purpose. Figure 4 shows the reflectivity of a glass substrate before and after depositing a 100 nm-thick Rf-6 film on its surface. The reflection from the backside of the substrate is not excluded in this measurement. By depositing the Rf-6 film, the reflectivity was reduced as much as 3.8% at the wavelength of 500 nm. Further improvement can be expected by optimizing the film thickness and by removing the reflection from the back side of the substrate.

4. Conclusions

It was shown that the fluoropolymer thin films can be prepared by the ion-assisted deposition polymerization of a fluoroacrylate monomer Rf-6. The film had low refractive index and low surface energy, and was attractive for antireflective coating that also has antipollution characteristic. In addition, the ion bombardment effect enhanced the adhesion of film-substrate interface, and the IAD film had higher stability compared to the spin-coated film. Since the film can be prepared directly from the monomer without using organic solvents, this technique is applicable on the surface of variety of organic substrates. Such features can be attractive for preparing protective antireflective coating on flexible displays.

References

[1] T. Takagi, Thin Solid Films **92** (1982) 1.

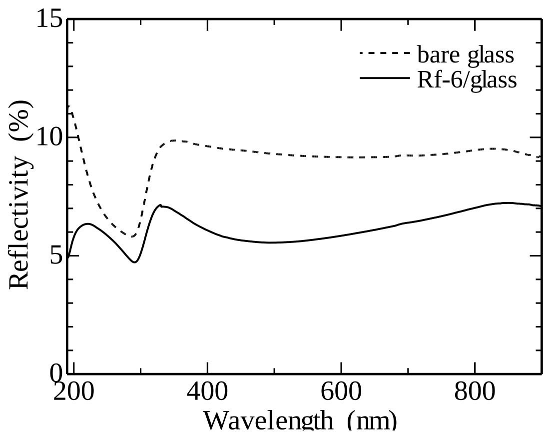

Fig. 4 Optical reflectivity of glass substrate before and after depositing the Rf-6 film by IAD.