



Ion-assisted vapor deposition of acryl polymer thin films

Kazuo Senda^{1,*}, Syunsuke Sotowa, Kuniaki Tanaka, Hiroaki Usui^{*}

Tokyo University of Agriculture and Technology, Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan

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ABSTRACT

Polymer thin films were prepared by an ion-assisted vapor deposition polymerization method that involves physical vapor deposition of monomer combined with low-energy ion irradiation. In a high vacuum environment, zinc diacrylate monomer was evaporated at a rate of 0.8 nm/min on gold-coated glass substrates under simultaneous irradiation by nitrogen ions of 20 nA/cm² at ion energy ranging from 500 to 2000 eV. The ion irradiation remarkably reduced the surface roughness of the deposited films. Infrared spectroscopy showed that the absorption bands of the vinyl group diminish with increasing ion energy. Formation of polymer molecules was confirmed by gel permeation chromatograph. Moreover, the film became insoluble to organic solvents when the ion energy was increased. These results indicate that polymer thin films can be prepared by vapor deposition of monomers under ion irradiation. The ion-assisted vapor deposition polymerization was also possible on insulating substrates.

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1. Introduction

Polymer coatings have wide applications in surface modification, protection, as well as decoration. Most of the conventional polymer coatings have been prepared by wet processes using polymer solutions or dispersions. The wet-coating processes have advantages in high throughput, large-scale applicability and cost effectiveness, which are important factors in mass-production. Although the wet polymer coating is a well-established technique, there still exist issues of handling insoluble materials, controlling the film/substrate interface, reducing defects such as pinholes, and more essentially, the use of organic solvents that can cause environmental pollution. On the other hand, recent advancement of functional polymers opened new application areas of polymer coatings in optical and electronic devices. For these applications, material purity and defect density are the first priorities. Many of the devices require nanometer-thick films and their multi-layered structures having well-defined interfaces. For such applications, the wet-coating methods cannot always satisfy the requirements in film quality.

Under these circumstances, the authors have proposed to prepare polymer thin films by means of vacuum-based physical vapor deposition (PVD) process [1]. In spite of its drawback in production cost, the vapor deposition is convenient in obtaining high-purity thin films in excellent controllability, which is important for device fabrication. The vapor deposition has been widely used for film formation of small organic molecules as well as metals and inorganic compounds. However, polymers that have high molecular weight

cannot be evaporated to employ the vapor deposition process except for limited materials such as low-molecular weight polyethylene [2] or polytetrafluoroethylene [3]. PVD of polymer can be realized by vapor deposition polymerization, evaporating small molecules that can be polymerized on the substrate surface. The vapor deposition polymerization was first reported as a solventless deposition method for polyimide thin films by coevaporating diamine and carboxylic acid dianhydride [4,5]. This concept can be utilized for preparing such polymers as polyurea [6], polyurethane [7], π -conjugated conductive polymer [8], and optically nonlinear polymers [9] that polymerize by stepwise reaction of two reactive monomers. Another class of vapor deposition polymerization is to employ chain reaction by evaporating vinyl or acryl monomers. This method has an advantage of obtaining high molecular weight polymers from single monomer species. The polymerization reaction can be induced by activating the monomer by such methods as hot filament [10], electron irradiation [11,12], ultraviolet (UV) light irradiation [13] or by thermal activation [14].

With a purpose to explore further possibility of developing a new PVD technique of polymer thin films, this paper reports the effect of low-energy ion bombardment in the course of vapor deposition of acryl monomers. Compared to the UV and electron irradiation, which primarily cause electronic excitation of the molecules, low-energy ions interact with the target molecules mainly by nuclear collision. Low-energy ion irradiation is frequently used for surface treatment such as sputter cleaning and chemical modification of the substrate surface. For film deposition, low-energy ion bombardment is known to bring about such effects as shallow implantation, formation of interlayer, enhancement of surface migration, and creation of nucleation centers [15]. These features have been utilized to enhance crystal growth and to improve film characteristics for the vapor deposition of non-reactive small molecules [16,17], but not to induce

* Corresponding authors.

E-mail address: h_usui@cc.tuat.ac.jp (H. Usui).

¹ On leave from Sumitomo Precision Product Co., Ltd.

polymerization. As for the polymerization reaction, irradiation of high energy ions to vapor-deposited small molecules was reported to induce solid-phase polymerization and carbonization [18]. On the other hand, no attempt has been made to prepare polymeric thin films by simultaneous irradiation by low-energy ions during vapor deposition of polymerizable monomers. Such an ion-assisted vapor deposition polymerization can be attractive as a new solvent-free polymer coating method that incorporates surface modification with polymer growth.

2. Material and methods

Zinc diacrylate (ZnAc), shown in Fig. 1, was used as the monomer material for evaporation. ZnAc is a bifunctional acrylate monomer that can form stable polymer having network structure, and is frequently used as a crosslinking reagent for stabilizing the polymer structure [19,20]. The material purchased from Aldrich was used as received. Fig. 2 shows the schematic diagram of the ion-assisted vapor deposition system. The ZnAc monomer was evaporated from a Knudsen-type evaporation cell having an aperture of 1 mm diameter. The deposition was achieved for 1 h at an evaporation temperature of 210 °C. The deposition rate, monitored with a quartz crystal microbalance, was about 0.8 nm/min. During the vapor deposition, nitrogen ions generated from an electron-bombardment type ion source (SPECS IQE10) was irradiated to the substrate surface. The ion current, measured on the substrate holder of 5 cm square, was adjusted to 0.5 μ A, and the ion energy was controlled by applying an ion acceleration voltage (V_a) of 0 to 2000 V to the ion source. At V_a of 0 V, no ions were extracted from the ionizer, and no significant current was detected on the substrate holder. The quartz microbalance was installed in a position where ions do not impinge. The background pressure of the deposition chamber was 1×10^{-4} Pa, which increased to 1×10^{-3} Pa during the ion irradiation. The substrate was located at 20 cm from the evaporator and 6 cm apart from the ion source. Its temperature was kept at room temperature. As for the substrate, slide glass plate was cleaned with organic solvents and was coated with 10-nm thick chromium followed by 100-nm thick gold by vapor deposition. A commercially obtained 50 μ m-thick foil of poly(ethylene terephthalate) (PET) was also used as a substrate.

The surface morphology of the deposited films was examined by a scanning probe microscope (SPM) (KEYENCE VN-8000) in dynamic force mode. The chemical structure of the film on the gold surface was investigated by infrared (IR) absorption spectroscopy measured by reflection-absorption mode at an incidence angle of 80° (HORIBA FT-700 combined with reflection unit FX-305). On the PET substrate, IR spectrum was measured by the attenuated total reflection (ATR) method at an incidence angle of 45° using HORIBA FX-401 unit and a zinc selenide prism. When possible, the deposited film was dissolved in tetrahydrofuran (THF), and was analyzed by gel permeation chromatograph (GPC) (SHIMADZU LC-10 AD combined with CTO-10AS and SPD-10AU units) to measure the molecular weight.

3. Results

3.1. Surface morphology

The conventional vapor deposition formed thin films of ZnAc monomer, where ZnAc molecules condensed without chemical

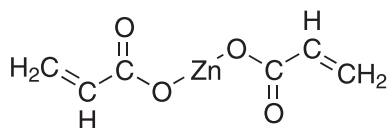


Fig. 1. Structural formula of zinc diacrylate (ZnAc) monomer.

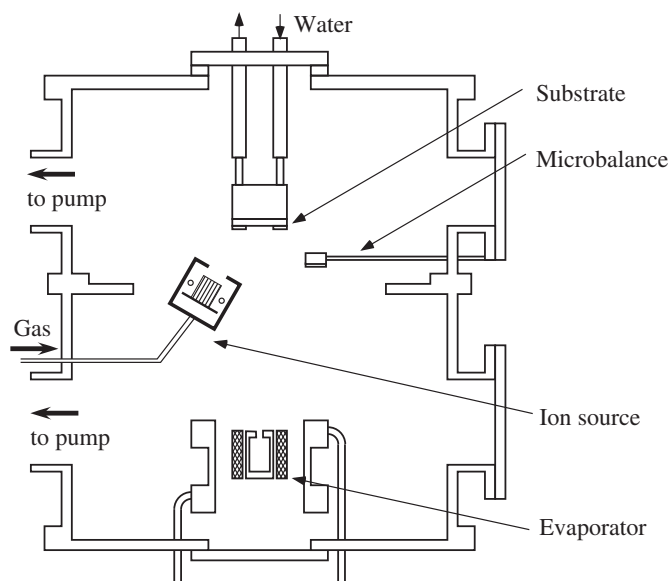


Fig. 2. Schematic diagram of the ion-assisted vapor deposition system.

reaction on the substrate surface. Since the vapor-deposited ZnAc films consisted of small molecules, it crystallized to give granular surface. On the other hand, the ion irradiation during the deposition caused a marked difference in the film morphology. Fig. 3 plots the film thickness and the arithmetic average surface roughness (R_a) of the films deposited on the gold surface as a function of ion energy. As a result of ion irradiation, the surface roughness decreased drastically and films of specular surface were obtained, whereas the film deposited without ion irradiation had a hazy surface. The film deposited without ion irradiation had R_a of 23.3 nm, which decreased to 2.8 nm by the ion irradiation at 500 eV. Further increase of ion energy decreased R_a to 1.8, 1.3 and 0.9 nm at V_a of 1000, 1500, and 2000 V, respectively. Meanwhile, the film thickness decreased with increasing ion acceleration voltage, although the amount of ZnAc evaporated was kept constant by monitoring with the quartz crystal microbalance.

Fig. 4 compares the SPM images of the films deposited on the gold surface without ion irradiation (a) and with the ion-assisted deposition at V_a of 2000 V (b). The former film had high density of hillocks that reflect the polycrystalline nature of the monomer film, while the film by ion-assisted deposition had flat and uniform surface. A preliminary adhesion test using a Scotch tape revealed that the film by the simple vapor deposition can be peeled off easily, while the adhesion of the ion-assisted film was improved by increasing V_a . The

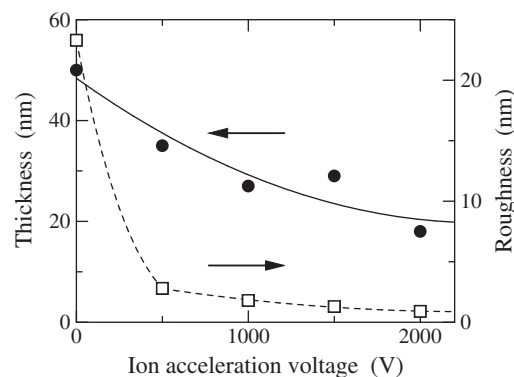


Fig. 3. Film thickness and arithmetic average surface roughness R_a of the films plotted as a function of ion energy of surface bombardment.

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