THERMAL ANALYSIS OF ORGANIC THIN FILMS

TATSUO NOMAKI, AKIKO YAMANAKA and KATSUYUKI NAITO

Toshiba Research and Development Center, Toshiba Corporation,
Saiwai-ku, Kawasaki 210, Japan

Abstract - Thermal analysis of a ultra-thin film has been studied by a new sample preparation technique. This paper shows this method and its application to Langmuir-Blodgett(LB) film. Detailed study on LB film were carried out by differential scanning calorimetry(DSC). Using this method, phase transitions in Cd-stearate LB films could be clearly observed.

Key words Langmuir-Blodgett film, cadmium stearate, thin film, thermal analysis, differential scanning calorimetry

In recent years, there has been much interest in the deposition of organic thin films, such as LB films. These films can be used extensively as resists, memories, sensors and other application in electronic devices. Therefore, precise characterization was required. In previous reports [1-3], much attention had been paid to structural studies. Also, thermal analysis has made marked progress in regard to the study on thin film [4]. However, as indicated in previous reports, the thin films were directly deposited on glass plate or metal foil (0.1-1mm). Therefore, the film to substrate volume ratio was extremely small. As a result, most of the work had been done on thin films in excess of 100nm thick. In order to study very thin film, such as LB film, the authors proposed a new sample preparation technique.

EXPERIMENTAL

Preparation method

A substrate design is shown in Figure 1. The silicon wafer was 5 inches in diameter. The organic thin film was deposited onto the wafer, which was coated with Au film. The Au film was formed by vacuum deposition technique in 100-200nm thickness range. As sample for thermal analysis, the organic thin film with Au film was removed from the wafer with a razor-edge.

LB films deposition

Cd-stearate films (5-21 layers) were deposited onto the Au/wafer substrates by the LB method. A chloroform solution of Cd-stearate was spread on a subphase of pH=5.8-6.0 and $[Cd^{2+}] = 1mM$ at 20°C. The films were deposited under a surface pressure of 25 dyne/cm at a 5mm/min speed, and then dried in nitrogen atmosphere.

Fig.1
Substrate design for
thermal analysis on thin films

a:Organic thin film
b:Au film
c:Silicon wafer

Thermal analysis

Thermal analysis was carried out by differential scanning calorimetry (DSC). The DSC data were collected with DSC 100 model (Seiko Instrument Inc., Tokyo) at a 5K/min heating and cooling rate in N_2 flow. The DSC apparatus capability was checked with indium and stearic acid. LB films, with Au film removed from the silicon wafer, were used as samples in the 0.1–0.2 mg range.

Results and discussion

Cd-stearate films in 5–21 layers were prepared by the LB method. The 11–12mg samples were measured by DSC. In the case of 5 layers, the LB film was approximately 12.5nm in thickness, and net weight was approximately 0.05mg. The authors obtained clear DSC curves in 5–21 layers. Figure 2 shows DSC curves in Cd-stearate LB films (15 layers). In the case of heating curve (a), the endothermic peak observed in the 80–110 °C range, which corresponds to the phase transition for melting. Another weak peak was also observed at nearly 70 °C. As mention below, this peak was assigned to the melting of stearic acid as the an impurity. In the cooling curve (b), the exothermic peak in recrystallization was observed at nearly 90 °C. This sample preparation method is also applicable to the structural study by the IR reflection method. As Au film is effective to increase the infrared ray reflectance, clear IR spectra can be obtained for the LB films. Figure 3 shows the IR spectrum for Cd-stearate LB film (15 layers). IR spectra were collected with a BIO-RAD DIGILAB FTS-60A fourier transform IR spectrometer, using the grazing incidence reflection method. The band around 1700 cm^{-1} corresponds to stretching vibrations for bond C=O in the COOH group. This result strongly suggests that the endothermic peak (nearly 70 °C) in DSC corresponds to the melting of stearic acid in the LB films. Intense bands of symmetric stretching vibration (ν_s): 1432 cm^{-1} and asymmetric stretching vibration (ν_a): 1548 cm^{-1} of COO^- group were also observed.

Fig.2 DSC thermogram for Cd-stearate LB film (15 Layers)

(a) Heating curve
(b) Cooling curve

Fig.3 IR spectra for Cd-stearate LB film (15 Layers)

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