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Mechanical properties and densification behavior of pentacene films pressurized by cold and warm isostatic presses

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ABSTRACT

Mechanical properties such as bending strength represent critical issues for the manufacture and practical use of flexible organic semiconducting films. In this study, we have used isostatic presses to densify pentacene films and compared the densification behavior and mechanical properties of the films. Although most pores formed between the grains were crushed in the pressed films, thickness reduction of the films was nondetective. And the nondetection is attributed to original dense cylindrical structure of the as-coated films which is predicted to produce a porosity 9.3% and a thickness reduction 80 nm. Both the indentation modulus (15.0 GPa) and the indentation hardness (0.643 GPa) of the as-coated films were reduced by up to 25% and 23% in the WIP films. The resultant critical bending radius of the WIP films of 4.29 mm is approximately the same as that of the as-coated films because of simultaneous falls in both modulus and hardness. The decreasing modulus and hardness in the isostatically pressed films are concluded to be caused by relaxation of the pentacene grain anisotropy accompanied by buckling of the grains.

1. Introduction

Flexible organic semiconducting films (OSFs) are promising materials for use in electrical devices including organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) cells, and organic thin film transistors (OTFTs) because OSFs are characterized by high bending strengths and a diverse selection of materials. In addition to these advantages, these OSFs are expected to be manufactured using costless continuous processes such as roll-to-roll large-scale production [1], unlike the costly photolithography batch processes used for conventional silicon inorganic semiconductors. However, because of the low electrical properties of OSFs, only a few OLED displays made using low-molecular-weight OSFs have been made into consumer products, and most OSF-based devices are still being studied to improve their electrical properties. For example, although a maximum photoelectric conversion efficiency (PCE) of 6.4% has been reported for a low-molecular-weight OPV cell [2], a PCE of more than 10% is generally considered to be necessary for practical applications. Therefore, the electrical properties of OSFs are a most important issue that must be immediately resolved for practical applications.

While considerable attention has been paid to the improvement of OSF electrical properties, it is also important to investigate the mechanical properties of the OSFs that are closely related to their bending behavior [3,4], because flexible OSFs may be exposed to bending strains in the roll-to-roll manufacturing process and subsequent

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practical applications. Kanari et al. [5–7] have examined the mechanical properties of OSFs by nanoindentation (NI) testing and have also proposed a prediction equation for the critical bending radius at which an OSF on a flexible substrate is plastically broken. They also found that the mechanical properties of OSFs are affected by the internal film geometries and the arrangement of the grains. In addition, OSFs necessarily contain pores inside the films and at the film/substrate boundaries, because the vacuum evaporation coating method used for low-molecular-weight OSFs vaporizes the raw molecules as a cluster rather than as a single molecule, and then the pores are formed between the molecule clusters that are adhered to the substrate. Similarly, alternative wet coating methods for polymeric OSFs, such as spin coating, dissolve the raw molecules into a solvent and then pores are left behind at every location where the solvent vaporizes. Fig. 1 shows a scanning probe microscope (SPM) image of the grains and numerous pores formed in a metal-free phthalocyanine (H_2Pc) film. By densifying the OSFs by crushing the physically empty pores, we can probably improve the mechanical properties of the films. Because the pores also significantly degrade the electrical properties of OSFs [8], uniaxial pressurization of the films during the nanoimprinting process [9–13] has improved the electrical properties of the films. However, the uniaxial contact pressure provided by the flat stamp is necessarily non-uniform, discontinuous, and unrepeatable. For example, if a flat stamp pressurizes an OSF device that is 100 nm thick and 100 μm wide [14] with an inclination of 1/100 during the nanoimprinting process, the height difference between the two ends of the device is 1 μm, which is ten times the device thickness. Kanari et al. [15] have used a cold isostatic press (CIP) process on a phthalocyanine (H_2Pc) film (1050 nm thick) to densify the film by crushing the pores at a densification ratio of 40%. Because the CIP naturally applies a hydrostatic contact pressure that is both constant and continuous on the films, it can wholly crush the pores in the films while maintaining geometrical similarity, even for multilayered OSFs. As a result of the CIP processing, the H_2Pc films were improved in terms of their elastic modulus, hardness, and bending strength by factors of 2.3 times, 2.8 times, and 26%, respectively. Although the availability of the CIP process has been manifestly proved to improve the mechanical properties of a low yield strength (σ_y = 54 MPa) H_2Pc film, the effects of the CIP process must also be investigated for relatively high yield strength OSFs.

Pentacene is a promising material for OTFTs because of its high mobility. In this study, we examine the effects of the CIP process on pentacene films that have high σ_y (215 MPa). The pentacene films are also subjected to warm isostatic pressing (WIP) to ensure sufficient pressing effects, because the σ_y of these pentacene films is slightly higher than the maximum pressure of an isostatic pressing instrument (200 MPa). The surface morphology, thickness, elastic modulus, and hardness of the films are measured before and after the isostatic pressing processes to quantitatively investigate the effects of these presses on the geometrical structures and mechanical properties of the films. The bending strengths of the films are also calculated based on the measured mechanical properties.

2. Experimental

For comparison, three kinds of pentacene films were prepared: an as-coated film, a CIP processed film, and a WIP processed film. Pentacene raw materials (Sigma–Aldrich P1802) were purchased and used without any subsequent treatment. The pentacene films were each coated on a glass substrate (6.0 GPa hardness) at room temperature by vacuum evaporation with a deposition rate of 0.15–0.3 nm/s and vessel pressure of 10^{-4} Pa. As shown in Fig. 2, the CIP films were previously vacuum sealed into doubled polyester (PE) bags (100 μm thick) to prevent them from coming into contact with the pressurizing water and they were then pressed in a pressure vessel after the pressurizing water in the vessel was confirmed to be continuously maintained at room temperature for at least 30 min. In contrast, the WIP films that were installed in the pressure vessel were heated using an electric heater and then pressed in the same manner as the CIP films immediately after the pressurizing water in the vessel was confirmed to be continuously maintained at a temperature of 80 °C for at least 30 min. The heating temperature

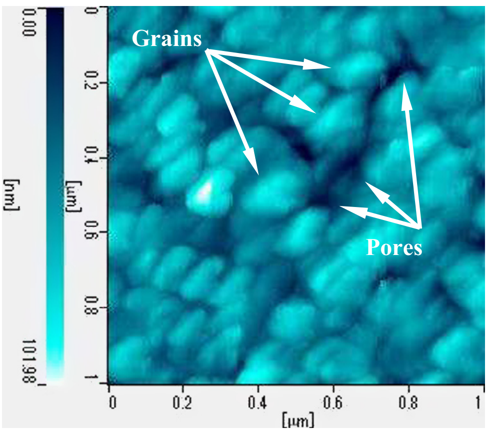

Fig. 1. SPM image of the open pores formed in an H_2Pc film surface.

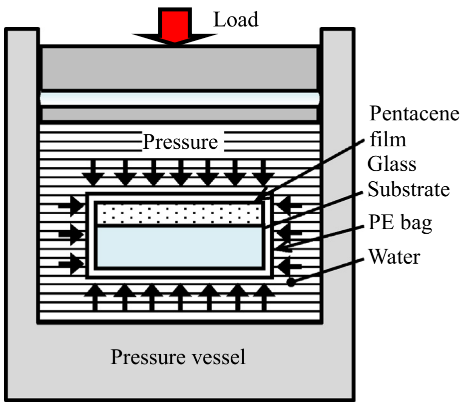

Fig. 2. Schematic drawing of a pentacene film sample installed in a pressure vessel during CIP and WIP processes.