Improvement of Mechanical Property of Indium-tin-oxide Films on Polymer Substrates by using Organic Buffer Layer

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This paper gives the basic mechanical properties of indium-tin-oxide (ITO) films on polymer substrates which are exposed to externally and thermally induced bending force. By using modified Storey formula including triple layer structure and bulge test measuring the conductive changes of patterned ITO islands as a function of bending curvature, the mechanical stability of ITO films on polymer substrates was intensively investigated. The numerical analyses and experimental results show thermally and externally induced mechanical stresses in the films are responsible for the difference of thermal expansion between the ITO film and the substrate, and for substrate material and its thickness, respectively. Therefore, a gradually ramped heating process and an organic buffer layer were employed to improve the mechanical stability, and then, the effects of the buffer layer were also quantified in terms of conductivity-strain variations. As a result, it is uncovered that a buffer layer is also a critical factor determining the magnitude of mechanical stress and the layer with the Young's modulus lower than a specific value can contribute to relieving the mechanical stress of the films.

Keywords : SI transition , BSCCO, Mixed crystal, Thin film, KT transition

1. INTRODUCTION

Organic For more than a decade now, organic electron devices based on polymer substrates have been envisioned as a viable alternative to more traditional, mainstream electron devices based on inorganic substrates such as glass and silicon substrates[1,2]. Hence, organic thin-film devices have been studied extensively and thus the tremendous progress in performance of these devices has been achieved[3-5]. There are many problems, however, such as stress-induced electro-mechanics of metallic films, interfacial mismatch of between organic and inorganic materials, chemical compatibility of the hybrid materials, and etc [6-7]. Most of all, the stress-induced mechanical degradation of metallic films has been considerably researched, since it was connected with the device performance directly[8-10].

In this paper, in addition to the novel methods for the reduction of thermal stress in ITO films, we present a new physical model of the externally induced mechanical stress taking into account a neutral layer which is stress-free layer in a film-substrate couple. To essen the externally induced mechanical stress, we employ a buffer layer which is inserted between the films and the polymer substrates, and then the effect the buffer layer are intensively studied with numerical analyses and experimental results. The detailed perimetal setup and results of the deposition of reliable ITO or metal films have been studied, and processing concerning the polymer substrates has reported earlier[11-13].

2. EXPERIMENTAL

RF-magnetron and DC sputtering systems, we were modified for these studies, performed deposition of ITO films on polymer substrates. Deposition process was carried out at a relatively temperature (100°C) for reducing the thermal expansion of the polymer substrates. Buffer layers were prepared on the bare polymer substrates with the deposition methods such as spin coating and sputtering systems. Organic buffer materials used in the experiments polycarbonate, polyimide and acrylic material and inorganic buffer material is aluminum (Al) metal, to the buffer layer and the ITO films deposition.
Trates were treated with pre-heating at 150°C and oating of hexamethyldisilazane (HMDS) for sing water vapor or gases embedded in a polymer x and improving the adhesion property of the buffer er, respectively.

Film structures are processed on planar thin substrates of polycarbonate, with a typical ness of 100, 180 and 200-μm thicknesses. The substrate couple is placed over a rectangular hole clamped by a ring. The pressurized gas is then used form the couple into the shape of cylindrical, which carried out using a miniature mechanical testing ine. A straightforward calculation can estimate the of curvature. The stress-strain relations are stored by measuring the variations of electrical nance in ITO films in situ using a four-point surement technique as a function of bending cu.

The nano-indentation measurement is also per for the investigation of the Young’s moduli of buffer material and ITO films. The Young’s moduli a materials used in these experiments were estimated the difference of the initial module between the mer substrates and the film-substrate couples[14]. lly, each surface of ITO films is observed using an ZE microscope. All of the samples used in these ximents included 30 ~ 40 Ω/sq. in sheet resistance thickness of about 100 nm. The ITO films on PC trates were patterned for island arrays of 200 x 200 in size with spacing of 30 μm, and subsequentlyls were deposited, and then they were also patterned the pad-electrodes of reliable measurement. All of measurements were carried out with the surge located at the midpoint of the gauge. This island sture of ITO sample was prepared for the precise ysis of strain dependent conductive changes of the free of edge force effect resulted from the bulge.

The nano-indentation measurement is also performed the investigation of Young’s moduli of buffer rial and ITO films. The Young’s moduli of all rials used in these experiments were estimated from difference of the initial module between the polymer trates and the film-substrate couples.

3. RESULTS AND DISCUSSION

The thermal stress in metallic films on polymer substrate contrast to glass or silicon substrates, polymer trates have low thermal resistance, non-rigidness, k mechanical characteristics and high coefficient of all expansion (CTE). The CTE values of 44 ppm/K ES, 52 ppm/K in PET and 37 ppm/K in PC are an r of magnitude higher than those of the ITO films rted in other literatures. The difference in thermal expansion between polymer substrates and ITO films can cause serious tensile or compression stress, leading to cracks and delamination of the ITO films. In general the thermal stress in thin films on substrates can be expressed as the followings,

\[ \sigma_T = (\alpha - \alpha_f) \cdot T \cdot E_f / (1 - \nu) \]

\[ \alpha = \Delta \ell / \ell_0 \cdot \Delta T \cdot (K^{-1}) \]

where, \( \alpha \) is the coefficient of thermal expansion, \( \Delta T \) is the difference between zero-stress temperature and the current temperature, R is the curvature of the film-substrate couple, and \( E_f \) is young’s modulus of the thin film, respectively. From eq. (1), it is evident that the differences between CTE \( (\alpha - \alpha_f) \) and process temperature \( (\Delta T) \) are mainly responsible for the thermal stress imposed on the ITO films. The reduction of the difference in thermal expansion between polymer substrates and ITO films is required to lessen the thermal stress, since the process temperatures are fixed for the optimum conditions of ITO films and limited for the compatibility of polymer substrates.

Figure 1 shows the results of temperature-dependent dilatation measurements on suitable test vehicles, which were undertaken pre-annealing process below glass transition temperature of polymer substrate (\( T_g \)). As shown in Fig. 1, it is evident that glass materials show the thermal strain of an order of magnitude lower than polymer materials. The polymer substrates subjected to the temperature ramped with 10°C/min. shows larger thermal strain than that ramped with 5°C/min.. This fact indicates that the ramped heating process including gradual, or a stepped increase of temperature has a less effect on the polymer expansion. The characteristic of less temperature-dependent polymer expansions was also found in pre-annealing polymer substrates. From the

![Dilatation vs Elevated Temperature](image)
above results, it is concluded that the tensile stress imposed on ITO films on polymer substrates, which is originated from the thermal misfit between the ITO films and the polymer substrates, can be reduced by the ramped heating process. It is also derived from the results that if the additional inorganic films are deposited on the bottom side of substrate before the ITO films deposition, it may reduce the tensile stress in the ITO films during the deposition processing, lessening the thermal expansion of the polymer substrates. Therefore, if SiO₂ films, used as a gas barrier layer, deposited on the bottom side of the polymer substrate, it can reduce the thermally induced tensile stress.

3.2 Numerical analysis of externally induced mechanical stress in ITO films

When an external force is applied to the substrate, mechanical distortion causes the substrate to bend elastically and the bending curvature of the substrate depends on the thickness and the Young's modulus of substrate. We assume the substrate to be isotropic in the plane of the substrates. If polymer substrate is thin and compliant, a film-substrate couple bends into a cylindrical roll instead of a spherical cap. Hence, we ignore the coefficient of Poisson's ratio in following analysis. Under a specific tensile or compression force, a film-substrate couple bends with constant curvature of R. The bending momentum elongates the sheet in the upper section of the film-substrate couple and compresses the sheets in the lower section. Between the elongated and the compressed parts, there is a "neutral layer" at the position z₀ free from any stress. By this postulation, stress σ(z) can be obtained as the function of z₀. The neutral layer position of z₀ is derived from the condition that there is no net elongation force acting on the film-substrate couple.

\[
z₀ = \frac{t_s}{2} + \frac{R \cdot \sigma \cdot t_f}{E_s \cdot t_s}
\]

(3)

The stress and strain of film on the substrate bended with curvature of R can be expressed as

\[
\sigma(z) = \frac{E_s \cdot t_s^3}{6R \cdot t_f \cdot (t_s + t_f)}
\]

(4)

\[
\varepsilon(z) = \frac{t_s^2}{6R \cdot t_f \cdot (t_s + t_f)} \cdot \frac{E_s \cdot t_s}{E_f \cdot t_f}
\]

(5)

The strain of a ITO film on a substrate can be described as the functions of Eₓ/Eᵧ and tₓ/t Sentry. In the case of polymer substrate, the value of Eₓ/Eᵧ is much smaller than that of glass or silicon substrate (in polymer substrate: Eₓ/Eᵧ ≈ 0.05 ~ 0.005, glass or silicon substrate: Eₓ/Eᵧ ≈ 3 ~ 1). It suggests that the strain imposed on the ITO can be lessened with polymer substrate at the bending curvature.

If buffer layer is inserted between thin ITO film polymer substrate as shown in Fig. 2, the mechanism stress-strain relation in triple layers can be analyze the same manner but it is too lengthy and complex. The thickness and Young's modulus of buffer layer postulated as tₓ and Eₓ respectively. In the case of the sheet containing buffer layer, stress-strain relation can analyze respect to triple layer structure. This study leads the neutral layer position to

\[
z_n = \frac{E_s \cdot t_s + E_b \cdot (t_s + t_b)}{2 \cdot (E_s + E_b)} + \frac{R \cdot \sigma \cdot t_f}{(E_s + E_b) \cdot t_s}
\]

As shown in eq.(6), inserting a buffer layer including the Young's modulus of Eₓ can change the position of neutral layer. In the case of Eₓ = E_s and tₓ << t_s, we obtain the neutral layer position: moves toward ITO by tₓ/4 compared to a film-substrate couple without buffer layer. Furthermore, in the case of Eₓ ≠ E_s and tₓ, as the value of Eₓ decrease, the position of neutral layer shifts from mid-surface toward thin film accompanies with diminishing of stress imposed on film. From the above equations, we can obtain the same formula on film-substrate structure containing buffer layer. The result is given in eq. (7)

\[
\sigma(z) = \frac{E_s \cdot t_s^3 \cdot \beta}{12 \cdot R \cdot t_f \cdot (t_s + t_f + \frac{t_f - \alpha}{2})}
\]

Where,

\[
\alpha = \frac{E_s \cdot t_s + E_b \cdot (t_s + t_b)}{2 \cdot (E_s + E_b)}
\]

and

\[
\beta = 2 \cdot E_s \cdot \alpha \cdot t_s \cdot (t_s + \alpha) - E_b \cdot [(t_s + t_b - \alpha)^3 - (t_s + t_b - \alpha)^2]
\]
most of applications for thin film electron device, the properties of ITO films are fixed to their optimum electrical, optical, and chemical properties. Hence, under constant bending strain, stress in ITO film with buffer layer is determined by the Young's modulus and thickness of buffer layer and polymer substrate. From the eq. (7), it should be noted that buffer and substrate including thinner thickness and lower Young's moduli are able to reduce the stress in film on polymer substrate.

Reduction of externally induced mechanical stress in ITO films using organic buffer layer
suggests the changes in resistance as a function of bending curvature, which results from the externally induced mechanical force. Therefore, we provide a model that reduces the amount by which the electrical resistivity of ITO film changes with the imposed strain. Since a film–substrate couple is bent by different mechanical strain, the difference in mechanical strain be expressed as a function of bending curvature. Moreover, the stress imposed on ITO films can be indicated by an increase of electrical resistivity resulting from delaminating and cracks. According to eq. (7) because the Young's modulus of substrate is one of the factors determining mechanical stress, we choose polycarbonate foil as a substrate for its lower Young's modulus and availability. Fig. 3(a) shows the stress strain relations of indium-tin-oxide (ITO) films on polymer substrate with various polymer buffer layers. It depicts the changes in electrical resistivity as a function of bending curvature. In the cases, the values of resistivity in ITO films are changed with buffer material at the same bending curvature. The results obtained experimentally are in excellent agreement with the predictions supposed in previous modeling. In the cases of constant thickness of buffer layer and ITO film on the same substrate, stress imposed on thin film depends on a value of eq. (12).

From these experiments, it is clear that using buffer layers, the increment of resistivity of ITO layer is

![Graph](image_url)

3. (a) shows the dependence of electrical resistivity increment of ITO films on bending curvatures and buffer materials, and (b) shows the dependence of electrical resistivity increment of ITO films on bending curvatures substrate thickness.

![Graph](image_url)

Fig. 4. (a) shows the dependence of electrical resistivity increment of Ta films on buffer material when they are exposed to external compressive force, and (b) shows dependence of electrical resistivity increment of Ta films on buffer material when they are exposed to external tensile force.
suppressed, which means that the stress is somewhat relieved by the buffer layers. (assuming that resistivity is increased by the cracks in the film, caused by the stress). Furthermore, the experimental results show the changes of electrical resistivity are reduced by buffer material including lower value of Young's modulus in accordance with our numerical analyses. Fig. 3(b) shows the dependence of stress-strain relation in ITO films on the thickness of polymer substrates, indicating that the stress in the film-substrate couple also can be controlled with the variation of the substrate thickness. From Fig. 3(b) and eq. (7), it is clear that the stresses in the ITO films are relieved more with the thinner substrate.

Another conductive material used for the experiment is tantalum (Ta) metal which is promising material for the area of integrated circuit and flat panel display. Figure 4 (a) shows the stress-strain relation of Ta film on polymer substrate with various buffer layers. The material used for the buffer layers are polycarbonate film (E_s: 2.1 Gpa) and aluminum film (E_s: 11.5 Gpa) of 0.5 μm thick, respectively. Furthermore, it is also found that the stress imposed on Ta films is much larger under tensile stress than under compressive stress. It is considered that deposition process inevitably imposes tensile stress on the films, since polymer substrate has higher thermal expansion than that of the films. Therefore, externally induced compressive force reduces the tensile stress, but externally induced tensile force increases the stress in the Ta films by adding additional tensile stress to the intrinsic tensile stress. Figure 4 (b) shows the stress-strain relation of Ta films under external tensile force. Compared to Fig. 4(a) and (b), it is evident that the tensile force imposes 7 ~ 8 times more stress on Ta film than that of compressive force. It is also found from previous simulation using eq. (7) that the maximum Young's modulus of buffer layer for application to reduction of stress has not to exceed 2.885 giga-Pascals (10^9 Pascal). It was calculated with \( E_s, b_0, f_r \) and \( E_f \) are 100 μm, 0.5 μm, 0.1 μm and 5.3 Gpa, respectively, under vening curvature of R. This means that buffer including Young’s modulus less than 2.885 Gj required to relieve the mechanical stress in ITO films. Fact well coincides with our experimental result showing an applicable Young's modulus of buffer for the improvement of the mechanical properties.

The measured Young’s moduli of buffer layers metallic films are shown in Table 1. Figure 5 show increase of cracks in the ITO films on polymer substrates with bending curvatures. Images in Fig. 5 were obtaained in situ using a long focal length optical microscope charge-coupled device camera. The empirical result incorporated in a model of increasing resistivity according to the increasing cracks. As shown in Fig. metallic films with buffer layer show lower density cracks than that of the films without buffer layer at the same bending curvature. We think buffer layer play role of lessening mechanical stress imposed on metallic films by absorbing or dispersing the external forces.

Table 1. Young’s moduli of various substrates, buffer layers and metallic films measured by nano-indentation method.

<table>
<thead>
<tr>
<th>Item</th>
<th>Material, (thickness)</th>
<th>Young’s modulus, (Gpa.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PC (100 μm)</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>PES (100 μm)</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>PET (100 μm)</td>
<td>5.53</td>
</tr>
<tr>
<td>Buffer layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polycarbonate, (0.5 μm)</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Polyimide, (0.5 μm)</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Acrylic resin, (0.5 μm)</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Aluminum film, (0.5 μm)</td>
<td>11.5</td>
</tr>
<tr>
<td>Metallic film</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ITO film, (0.1 μm)</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>Ta film, (0.1 μm)</td>
<td>140</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In conclusions, this paper gives the basic mechanics of ITO films on polymer substrate, who exposed to externally and thermally induced bending force. At first, we performed a theoretical analysis of stress-strain relation of ITO films including additive buffer layer. Then, we proposed stepped heating process including more gentle heating slope and organic buffer layer in order to reduce the stress imposed on ITO films onto polymer substrate. Empirical results of stress-strain relations show that buffer layer including lower Young modulus and thinner substrate can reduce mechanical stress imposed on metallic films. From the simulation using modified Stoney formula, constitutive of th
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it is also uncovered that Young’s modulus and the existence of buffer layer and substrate are also major factors determining the value of mechanical stress.

REFERENCES