Improvement of Mchanical 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 Storney 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 evices based on polymer substrates have been nvisioned as a viable alternative to more traditional, nainstream electron devices based on inorganic ubstrates such as glass and silicon substrates[1,2]. ence, organic thin-film devices have been studied xtensively and thus the tremendous progress in erformance of these devices has been achieved[3-5]. There are many problems, however, such as stressed-nduced electro-mechanics of metallic films, interfacial nismatch of between organic and inorganic materials, hemical compatibility of the hybrid materials, and etc 6-7]. Most of all, the stress-induced mechanical egradation of metallic films has been considerably esearched, since it was connected with the device erformance directly[8-10].

In this paper, in addition to the novel methods for the eduction of thermal stress in ITO films, we present a ew physical model of the externally induced nechanical stress taking into account a neutral layer hich 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 effec the buffer layer are intensively studied with nume analyses and experimental results. The detailed perimental setup and results of the deposition o 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, w 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 expa of the polymer substrates. Buffer layers were prep on the bare polymer substrates with the depos methods such as spin coating and sputtering sys Organic buffer materials used in the experiments polycarbonate, polyimide and acrylic material 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 ing water vapor or gases embedded in a polymer ix and improving the adhesion property of the buffer r, respectively.

O film structures are processed on planar thin mer 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 arried out using a miniature mechanical testing hine. A straightforward calculation can estimate the s of curvature. The stress-strain relations are itored by measuring the variations of electrical tance in ITO films *in situ* using a four-point surement technique as a function of bending cur- re. The nano-indentation measurement is also per- ed for the investigation of the Young 's modulli of uffer material and ITO films. The Young's modulli l 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 al microscope. All of the samples used in these riments 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 subsequnetly Al s were deposited, and then they were also patterned the pad-electrodes of reliable measurement. All of measurements were carried out with the island ples located at the midpoint of the gauge. This island ture of ITO sample was prepared for the precise ysis of strain dependent conductive changes of the s free of edge force effect resulted from the bulge Nano-indentation measurement is also performed the investigation of Young 's modulli of buffer rial and ITO films. The Young's modulli 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

hermal 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 nal 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 film can cause serious tensile or compression stress, leadin to cracks and delamination of the ITO films. In general the thermal stress in thin films on substrates can b expressed as the followings,

$$\sigma_f = (\alpha_s - \alpha_f)\cdot \Delta T \cdot E_f/(1-\nu_f) \qquad (1)$$

$$\alpha = \Delta\ell/\ell_0 \cdot \Delta T \cdot (K^{-1}) \qquad (2)$$

where, α is the coefficient of thermal expansion, ΔT i the difference between zero-stress temperature and th current temperature, R is the curvature of the film-substrate couple, and E_f is young's modulus of the thi film, respectively. From eq. (1), it is evident that th differences between CTE $(\alpha_s - \alpha_f)$ and process temperature (ΔT) are mainly responsible for the therma stress imposed on the ITO films. The reduction of th difference in thermal expansion between polyme substrates and ITO films is required to lessen the therma stress, since the process temperatures are fixed for th optimum conditions of ITO films and limited for th compatibility of polymer substrates.

Figure 1 shows the results of temperature-dependen dilatation measurements on suitable test vehicles, whic were undertaken pre-annealing process below glas transition temperature of polymer substrate (T_g). A shown in Fig. 1, it is evident that glass materials sho the thermal strain of an order of magnitude lower tha polymer materials. The polymer substrates subjected t the temperature ramped with 10°C/min. shows large thermal strain than that ramped with 5°C/min.. This fac indicates that the ramped heating process including gradual, or a stepped increase of temperature has a les effect on the polymer expansion. The characteristic o less temperature-dependent polymer expansions was als found in pre-annealing polymer substrates. From the

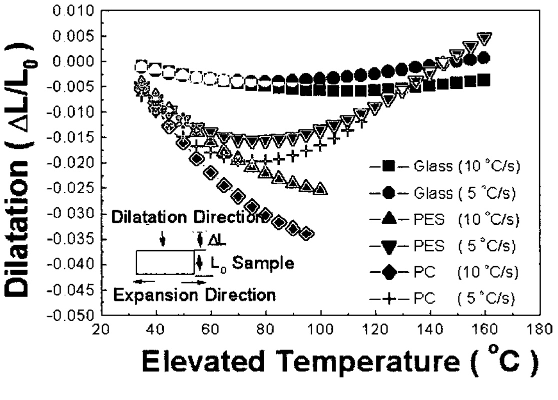


Fig. 1. Differences in thermal expansion of polyme substrates with heating slopes.

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 SiO_2 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 z_n free from any stress. By this postulation, stress σ(z) can be obtained as the function of z_n ,The neutral layer position of z_n is derived from the condition that there is no net elongation force acting on the film-substrate couple.

$$z_n = \frac{t_s}{2} + \frac{R \cdot \sigma_f \cdot t_f}{E_s \cdot t_s} \qquad (3)$$

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

$$\sigma_f(z) = \frac{E_s \cdot t_s^3}{6R \cdot t_f \cdot (t_s + t_f)} \qquad (4)$$

$$\varepsilon_f(z) = \frac{t_s^2}{6 \cdot R \cdot t_f \cdot (t_s + t_f)} \cdot \frac{E_s}{E_f} \cdot \frac{t_s}{t_f} \qquad (5)$$

The strain of a ITO film on a substrate can be described as the functions of E_s/E_f and t_s/t_f. In the case of polymer substrate, the value of E_s/E_f is much smaller than that of glass or silicon substrate (in polymer substrate: . E_s/E_f $\cong 0.05 \sim 0.005$, glass or silicon substrate : E_s/E_f $\cong$ (1). It suggests that the strain imposed on the ITO can be lessened with polymer substrate at the bending curvature.

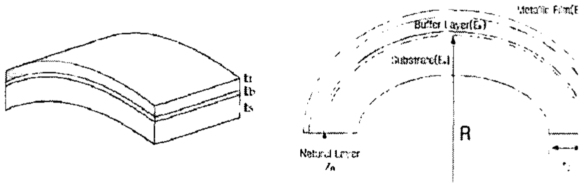


Fig. 2. Cross-sections of triple layer structure incl buffer layer.

If buffer layer is inserted between thin ITO film polymer substrate as shown in Fig. 2, the mechanis stress-strain relation in triple layers can be analyz the same manner but it is too lengthy and complic The thickness and Young 's modulus of buffer laye postulated as t_b and E_b , respectively. In the case o sheet containing buffer layer, stress-strain relation c analyze respect to triple layer structure. This stru leads the neutral layer position to

$$z_n = \frac{E_s \cdot t_s + E_b \cdot (t_s + t_b)}{2 \cdot (E_s + E_b)} + \frac{R \cdot \sigma_f \cdot t_f}{(E_s + E_b) \cdot t_s}$$

As shown in eq.(6), inserting a buffer layer inclu the Young 's modulus of E_b, can change the positic neutral layer. In the case of E_b = E_s and $t_f << t_s$, we obtain the neutral layer position moves toward ITO by $t_b/4$ compared to a film-substrate couple wit buffer layer. Furthermore, in the case of $E_b \neq E_s$ and t_s, as the value of E_b decrease, the position of ne layer shifts from mid-surface toward thin film accompanies with diminishment of stress imposed o film. From the above equations., we can obtain the s formula on film-substrate structure containing b layer. The result is given in eq. (7)

$$\sigma_f \cdot (z) = \frac{E_s \cdot t_s^3 - \beta}{12 \cdot R \cdot t_f \cdot (t_s + t_b + \frac{t_f - \alpha}{2})}$$

Where,

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

and

$$\beta = 2 \cdot E_s \cdot \alpha \cdot t_s \cdot (t_s + \alpha) - E_b \cdot [(t_b + t_s - \alpha)^3 - ($$

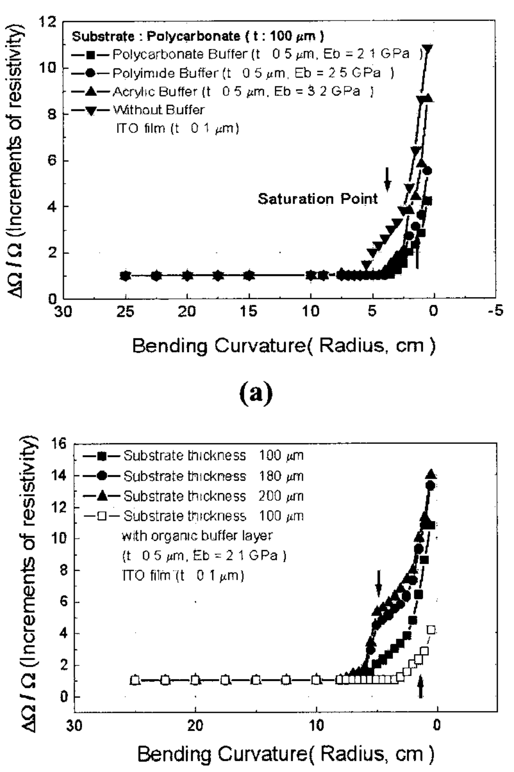
most of applications for thin film electron device, the kness and Young 's modulus of ITO films are fixed to their optimum electrical, optical and chemical erties. Hence, under constant bending strain, stress O film with buffer layer is determined by the Young odulus and thickness of buffer layer and polymer strate. From the eq. (7), it should be noted that buffer r and substrate including thinner thickness and lower e of Young 's modulli are able to reduce the stress in film on polymer substrate.

Reduction of externally induced mechanical stress in ITO films using organic buffer layer

e, we focus on the changes in resistance as a function strain, which results from the externally induced hanical force. Therefore, we provide a model that ribes the mechanism by which the electrical stivity of ITO film changes with the imposed strain. pose that a film–substrate couple is bent by different hanical strain, the difference in mechanical strain be expressed as a function of bending curvature.

Moreover, the stress imposed on ITO films can b indicated by an increase of electrical resistivity resulte from delaminating and cracks. According to eq.(7) because the Young 's modulus of substrate is one of th factors determining mechanical stress, we choos polycarbonate foil as a substrate for its lower Young ' modulus and availability. Fig. 3(a) shows the stress strain relations of indium-tin-oxide (ITO) films o polymer substrate with various polymer buffer layers. I depicts the changes in electrical resistivity as a functio of bending curvature. In the cases, the values o resistivity in ITO films are changed with buffer material at the same bending curvature. The results obtaine experimentally are in excellent agreement with th predictions supposed in previous modeling. In the cas of constant thickness of buffer layer and ITO film on th same substrate, stress imposed on thin film depends on value of eq.(12).

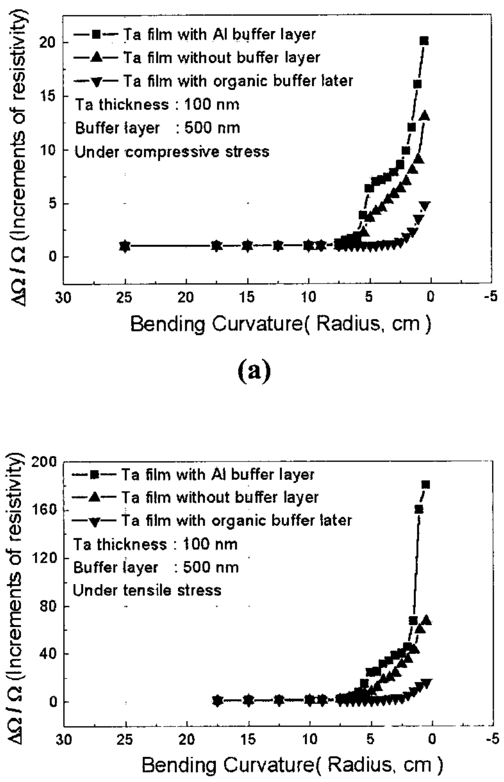
From these experiments, it is clear that using th buffer layers, the increment of resistivity of ITO layer is



(a)

(b)

3. (a) shows the dependence of electrical resistivity ement of ITO films on vending curvatures and buffer erials, and (b) shows the dependence of electrical stivity increment of ITO films on vending curvatures substrate thickness.



(a)

(b)

Fig. 4. (a) shows the dependence of electrical resisti increment of Ta films on buffer material when they exposed to external compressive force, and (b) shows dependence of electrical resistivity increment of Ta fi on buffer material when they are exposed to exte 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_b: 2.1 Gpa) and aluminum film (E_b: 11.5 Gpa) of 0.5 μm thick, respectively. Furthermore, it is also found out 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 ofTa 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 t_s, t_b, t_f and E_s are 100 μm, 0.5 μm, 0.1 μm and 5.3 Gpa. respectively, under vending curvature of R. This means that buffer including Young 's modulus less than 2.885 G required to relieve the mechanical stress in ITO films. fact well coincides with our experimental re showing an applicable Young 's modulus of buffer for the improvement of the mechanical properties.

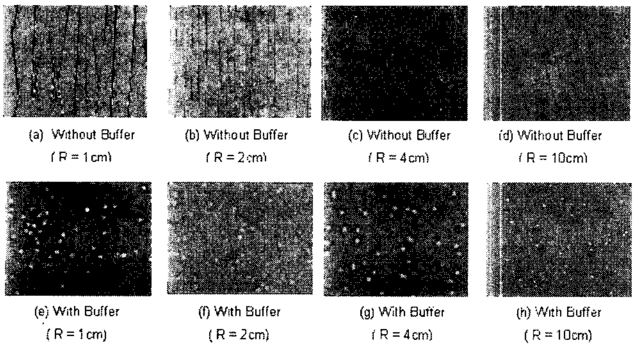

(a) Without Buffer (R = 1 cm)
(b) Without Buffer (R = 2cm)
(c) Without Buffer (R = 4cm)
(d) Without Buffer (R = 10cm)
(e) With Buffer (R = 1 cm)
(f) With Buffer (R = 2cm)
(g) With Buffer (R = 4cm)
(h) With Buffer (R = 10cm)

Fig. 5. Optical microscope images of crack appearing in ITO films in accordance with vending curvature and buffer layer substrates with heating slopes.

The measured Young 's modulli of buffer layers metallic films are shown in Table I. Figure 5 show increase of cracks in the ITO films on polymer subst with bending curvatures. Images in Fig. 5 were obt *in situ* using a long focal length optical microscope charge-coupled device camera. The empirical result incorporated in a model of increasing resis according to the increasing cracks. As shown in Fi metallic films with buffer layer show lower densi cracks than that of the films without buffer layer a same bending curvature. We think buffer layer pl role of lessening mechanical stress imposed on me films by absorbing or dispersing the external forces.

Table 1. Young 's modulli of various substrates, b layers and metallic films measured by nano-indent method.

Item	Material, (thickness)	Young 's modulus, (Gpa.)
Substrate	PC (100 μm)	5.3
	PES (100 μm)	5.7
	PET (100 μm)	5.53
Buffer layer	Polycarbonate, (0.5 μm)	2.1
	Polyimide, (0.5 μm)	2.5
	Acrylic resin, (0.5 μm)	3.2
	Aluminum film, (0.5 μm)	11.5
Metallic film	ITO film, (0.1 μm)	118
	Ta film, (0.1 μm)	140

4. CONCLUSION

In conclusions, this paper gives the basic ele mechanics of ITO films on polymer substrate, whi exposed to externally and thermally induced ben force. At first, we performed a theoretical analysis o stress-strain relation of ITO films including additi buffer layer. Then, we proposed stepped heating pr including more gentle heating slope and organic b layer in order to reduce the stress imposed on ITO f onto polymer substrate. Empirical results of stress-s relations show that buffer layer including lower You modulus and thinner substrate can reduce mecha stress imposed on metallic films. From the simul using modified Storney formula constituted of t er, it is also uncovered that Young 's modulus and ckness of buffer layer and substrate are also major tors determining the value of mechanical stress.

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