Nano- and Micro-Indentation of Photo-Patterned Spacers

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Abstract: *Micro- as well as nano-indentation has been carried out under various conditions. For instance, spacer patterns have been fabricated on inorganic and organic layers at the micro-fabrication laboratory in LG Chem, Ltd. where one can produce G2-sized color filter substrates. When indenting a spacer pattern on an inorganic layer that is composed of either indium-tin oxide or soda-free glass with negligible stress applied, its deformation is small enough to avoid substrate effects and its mechanical behavior seems to follow an intuitive trend. Under higher stress, substrate effects and interfacial phenomena start to affect the mechanical behavior. The external stress converges on the interface of the two layers to detach the pattern at the edge. Relaxation of stress leads to an abrupt change in deformation, which is observed as an inflection point in the load-unload curve. On organic layers such as overcoat films, black matrices, and color filter pixels, the mechanical behavior of a spacer becomes more complicated due to small difference in modulus between the spacer and the underlying organic layer. The results presented in this work can lead to more realistic insights on how spacers react against the external stress to maintain the quality of panels.*

Keywords: liquid crystal display; photo spacer; indentation; mechanical behavior.

Introduction

Mechanical properties of photo-patterned spacers have recently become of great interest nowadays. It is a general notion that they are closely related with the process window of one-drop filling of liquid crystal and the finger-tip reliability of liquid crystal display (LCD) panels. Widely-adopted methodology to scrutinize the role of spacers in enhancing the quality of LCD panels includes micro-hardness indentation of spacers. Resultant load-unload curves are used in order for extraction of so called elastic recovery rate in terms of either deformation or energy. Although many an experiment has been performed, few profound insights have been given due mainly to limited experimental conditions and the lack of knowledge on interfacial phenomena of layered thin films. Engineers and research scientists, therefore, ought to be dependent highly upon their cognitive reasoning. The field data are often deciphered with nothing more than the superficial description. In consequence of such an inductive reasoning, some crude images of the related phenomena mislead people to false conclusion.

In this work, micro- as well as nano-indentation has been carried out under various conditions. For instance, spacer patterns have been fabricated on organic (overcoat layers, black matrices, and color filters) and inorganic (soda-free glass and indium-tin oxide) layers in the micro-fabrication laboratory in LG Chem, Ltd. where people can produce G2-sized color filter substrates.

Results and Discussion

Indentation hardness: In general, the hardness of a material can be defined as different terms such as scratch, indentation, and rebound hardness. Indentation hardness has recently gained popularity because of the convenience and precision indenters can provide. The photo-spacer patterns are resulted from a couple of processes and so are the other organic layers. Highly needed are reliable criteria and methods to discriminate changes susceptible to process conditions that is too small to be recognized easily but that is large enough to affect the quality of an LCD panel. The test of indentation hardness thus came to be utilized. We used a nano-indenting apparatus, which was a product of MTS Systems Corporation. Four photo-spacer samples, denoted as PS 1 through 4, were prepared for the test. They are different only in photo-initiator composition, and the same components are used for the others such as binder polymers, cross-linking agent, solvent, and additives. The results are listed in Table 1.

Table 1. The indentation hardness of photo-spacer samples.

Sample	PS 1	PS 2	PS 3	PS 4
Indentation Hardness	0.32 GPa	0.33 GPa	0.33 GPa	0.36 GPa

Maximum load and elastic recovery: The micro-indentation test with a truncated tip (so called “flat tip”) has been applied to watch the behavior of photo-spacer patterns under external pressure. For instance, a photo-spacer pattern deforms as a flat-topped tip starts pushing it. Until the external load by the tip reaches a pre-determined value, it continues to shrink. The displacement corresponding to that load is called a maximum displacement and often indicated as h_{max}. When the external force is got rid of, the pattern recovers its original form to a certain extent. The difference between the heights before and after indentation is called a penetration depth and indicated as h_p, where the subscript “p” stands for penetration. The ratio of $h_{max} - h_p$ to h_{max} is called an elastic recovery rate and used as an indicator of how elastic we can think the pattern is. It is calculated from typical *F-d* plots of indentation (Figure 1).

By the way, the degree of elastic behavior can be defined also in terms of energy, W_e/W_t. W_e and W_t represent the work done by restoring force during un-loading process and the total work done by the external force during loading process, individually. Unlike the elastic recovery rate, the latter has the information on energy dissipation. Nevertheless, the elastic recovery rate is often introduced because its concept is simple enough for one to understand. Besides, it is considered to reflect the more realistic situation since the quality of an LCD panel is influenced by the deformation of patterns.

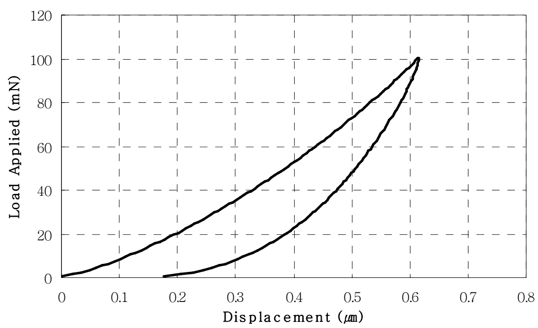

Figure 1. Typical plot of an *F-d* curve of indentation.

The results of the micro-indentation are shown in Figure 2. Top area was calculated according to the critical dimension at the 95% of the pattern height. As shown in Figure 2, there exist correlations among top area, h_{max} and elastic recovery. Contrary to the beliefs that most people have, it has been uncovered that the indentation hardness has no effect on the mechanical behavior of a photo-spacer pattern. This is because the indentation hardness only shows the property of the pattern surface. It, therefore, cannot represent the macroscopic behavior of a photo-spacer pattern. It seems plausible because, in the case of negative-type photo-resist, the most severe photo-reaction during exposure to UV light is expected to occur at the surface due to the high absorption coefficient of photo-initiators. The most influential factor was found to be the geometrical parameters of a pattern.

Multi-layer experiment: The color filter of LCD is a complex system that is composed of organic and inorganic thin films. For example, the color filter of the in-plane switching mode (IPS) consists of black matrices, color pixels, overcoat layer, and photo-spacer patterns on a glass substrate. All possible effects that may originate from various layers should be taken into account in order to imagine how photo-spacer patterns behave under external stress.

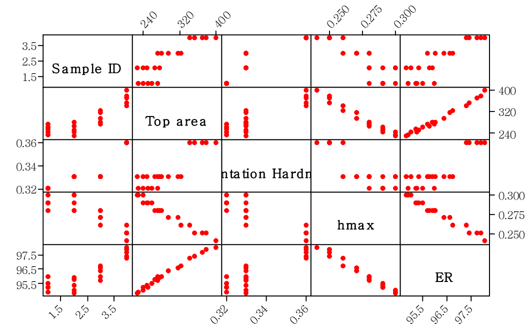

Figure 2. Matrix of scatter plots of sample ID, top area, indentation hardness, hmax and elastic recovery of a photo-spacer pattern.

In this work, photo-spacers were fabricated on a bare glass substrate, an overcoat-doped glass substrate, and on a prototypical color filter substrate for IPS mode application. As shown in Figure 3, the maximum displacement is the smallest in the case of patterns on a bare glass substrate. On the other hand, the *F-d* curves show identical features when an overcoat-doped and a color filter substrate were used. In the former case, it seems that the fairly high hardness of glass is reflected. When much softer matter is used as a substrate, the maximum displacement becomes larger as seen in the latter case. Besides, little difference in indentation behavior between the patterns on two organic substrates evidences that the substrate effect by the overcoat layer that is in direct contact with photo-spacer patterns is superior to that of the other underlying layers.

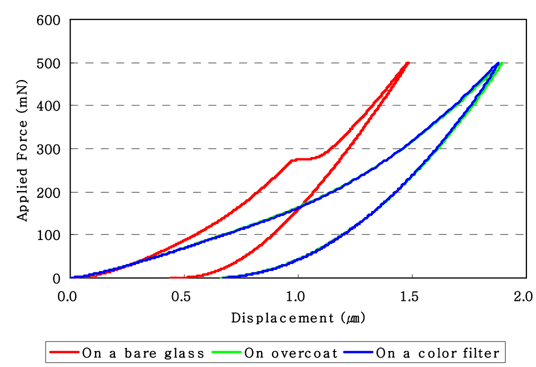

Figure 3. *F-d* curves for photo-patterned spacers on a bare glass substrate, an overcoat-doped glass substrate, and on a prototypical color filter substrate for IPS mode application.

Another interesting feature observed in Figure 3 is the inflection point of the curve for the photo-spacer on glass substrate. Many people misunderstand this feature as the point of yield where rupture occurs inside the pattern through severe change in configuration of the polymer network leading to permanent deformation. In fact this, however, merely supports the generally known idea that the adhesion at an organic-inorganic interface is weaker than the organic-organic counter part. It can be verified easily through observing the cross-section of the pattern that has been under great stress. Figure 4 shows the cross-section of the pattern that was made on a bare glass substrate that has been acquired through fast-ion bombardment and scanning electron microscopy.

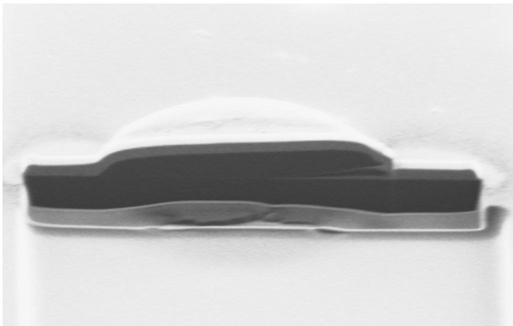

Figure 4. The cross-section of the photo-spacer pattern on an inorganic layer shows detachment at the organic-inorganic interface.

Summary

In this work, micro- and nano-indentation techniques were utilized to investigate the mechanical behavior of photo-patterned spacers. An interesting feature is that the macroscopic behavior of the pattern does not seem susceptible to surface hardness that is often used by mistake as the hardness of a material. It is rather subject to vary according to the change in the pattern shape. In addition, only the overcoat layer beneath photo-spacer patterns affects their indentation behavior. The inflection point on the *F-d* curve stems from the detachment of patterns at the organic-inorganic interface due to the weak interfacial interaction.