Dewetting Flow by Inter-surface Force during Hydrophobic Patterning

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1. Introduction

Recent development of organic semi-conductors enabled to fabricate Thin Film Transistor (TFT) by printing technology alone. Although many samples of printed TFT have been shown at trade-shows, it is hard to start mass-production because of printing accuracy. Ink jet printing is preferable because it has flexible alignment feature and can print TFT on demand. Problem of IJ technology is the trade off between productivity and drop size which is typically 10 micron. In contrast, typical TFT requires 5 micron gap between source and drain electrodes.

Photonic assistance or hydrophobic patterning was proposed to fill the gap of IJ accuracy and TFT requirement. It changes hydrophobic polymer surface to be wetted by hydrophilic IJ ink. Special hydrophobic polymer on a substrate is exposed by patterned UV light. Then its surface changes to hydrophilic by a chemical decomposition. This reaction has additional effect of shrinkage to combine chemical pattern and physical pattern. The IJ ink is printed roughly on the area, the ink dewets the hydrophobic surface and concentrate at the hydrophilic part. Accuracy of this process depends on dewetting behavior of the surface-ink system.

Analysis of patterned dewetting was done by A. Sharma et al. (1993,1996,2002) intensively, but they limit cases to very thin film on fine pattern for photo-lithography process. The process of printed electronics concerns much thicker film and coarse pattern of micrometer order. This study is to illuminate the dewetting phenomena for real printed electronics process including dewetting effect of solid surface morphology, Hamaker constant and liquid film parameters. Author adopts an extended Fowkes theory

(D.K. Owens, R.C.Wendt 1969) between a contact angle and dispersion, non-dispersion components of both liquid and solid. Also empirical relationship between surface energy components and Hamaker constant is used according to A. Sharma and G. Reiter(1996).

$$\Pi = \frac{a_H}{6\pi h^3} \quad (1) \qquad a_H = -24\pi d_0{}^2 \sqrt{\gamma_L^d}\left(\sqrt{\gamma_S^d} - \sqrt{\gamma_L^d}\right) \quad (2)$$

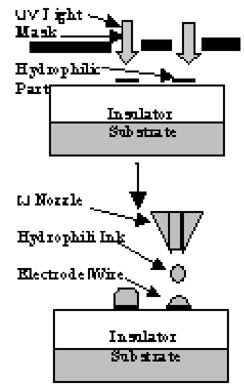

Fig.2-1 Process

2. Model

The most simple model to examine the dewetting hydrodynamics is evenly coated liquid film on a flat surface where a half is hydrophilic and a half is hydrophobic. Boundary of these two regions is a straight line and domain corresponds to a half of a pitch of line pattern. Well known Film-Profile Equation is used together with lubrication approximation. Here, pressure gradient includes not only gravity potential term and capillary force term but also gradient of Hamaker constant and the inter-surface force.

Before solving the model numerically, analytical formula is deduced. Dewetting flow stops when the capillary force balances intersurface force. Assuming surface shape as sinusoidal curve, a simple equation is deduced to show the parameter effect to the critical Hamaker constant. Finding is that the constant is proportional to the surface tension, fourth power of the thickness and square of the pitch inversely. (eq.5)

Numerical analysis is done with flat surface and hyperbolic tangent shaped terrace. Hyperbolic tangent shape can represent polymer shrinkage by UV and various ratio of line and space. Solutions are acquired by finite difference method and Euler integration. Basic parameters are 0.001Pa.s for viscosity, 0.02N/m for surface tension, 0.1 um for liquid film thickness, 50um for pitch and +/-10% step.

$$\frac{\partial \delta}{\partial t} = -\frac{\partial q}{\partial x} \quad (3) \qquad \frac{\partial p}{\partial x} = \rho g \frac{dh}{dx} - \sigma \frac{d^3 h}{dx^3} - \frac{1}{6\pi\delta^3}\frac{da_H}{dx} + \frac{a_H}{2\pi\delta^4}\frac{dh}{dx} \quad (4) \qquad a_H = \frac{(2\pi)^3 \delta^4}{p_W{}^2}\sigma \quad (5)$$

3. Numerical Results

Two major phenomena, wetting with deformed surface and dewetting are observed. Dewetting case shows rapid thinning at the hydrophobic side to indicate dewetting. There is a critical Hamaker constant to separate wetting and dewetting. Adding to this,

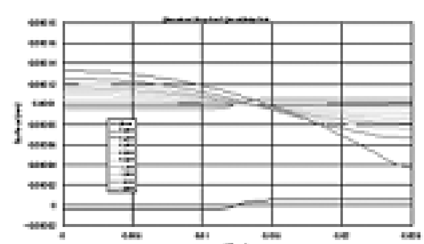
Fig.3-1 Typical numerical result

stronger dewetting cause droplet formation which is incomplete dewetting with liquid left behind on the hydrophobic part.

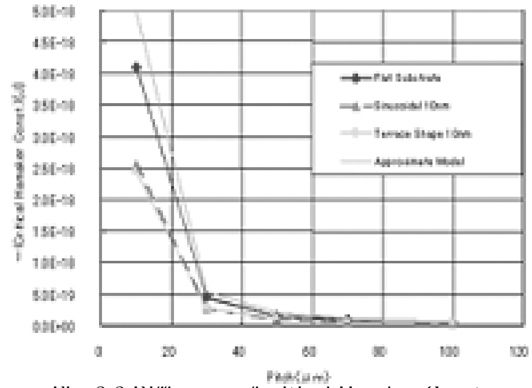

Fig. 3-2 Difference of critical Hmaker Const.

Author examined the effect of solid surface shape by replacing shape function of flat, sinusoidal and hyperbolic. Three surface shapes and approximate solution are compared in Figure 3-1. It is found that surface waviness does not affect much. Smaller pitch prevents dewetting. Absolute value of critical Hamaker constant increases 30% by the change of line and space ratio. Also it increases 20% for gradual slope at a step between a hill and a valley. Thus, surface morphology is not significant factor.

Effects of liquid parameters are examined. First, the effect of thickness to the critical Hamaker constant is found to be proportional to 3.82 power of the thickness, which is slightly different from analytical value of 4. Viscosity effect is theoretically less important to identify wettable and dewettable, because viscosity enters only in non-dimensional time and does not affect the equations. Inversely, the effect of surface tension is strong. Calculated critical Hamaker constant is proportional to the surface tension as same as analytical results.

Combination of wettability of hydrophilic part and hydrophobic part is various for real products. So, fate of the film on a combined surface of two Hamaker constants is interested. Figure 3-3, 3-4 shows flat surface case and hyperbolic shaped surface case to see the stability of the film. Horizontal axis corresponds to Hamaker constant of right side, vertical axis corresponds to that of left side. For terrace shaped surface, hill side is fixed to the right. In these figures, left/bottom is the most hydrophobic condition. For the flat surface, it is symmetry around center so the figure is symmetric around 45 degree line. It is found that the liquid dewets when right side Hamaker constant is more hydrophobic than $-2x10^{-19}$J even if the left side Hamaker constant is also hydrophobic as far as two constants are different. When the surface is too hydrophobic, incomplete dewetting occurs to form droplet. Figure 3-4 is basically similar to flat surface case except drop formation with hydrophobic part at the valley of the terrace. Weak effect of the surface shape appears to change the critical Hamaker constant to 1×10^{-19}.

4. Discussion and Conclusion

Parameter study of the dewetting process on hydrophobic/hydrophilic surface found that the process is controlled by a competition of capillary force and intersurface force. Also the results suggest that large difference between two Hamaker constants is not necessary but reasonable hydrophobicity is necessary. Reason of wider area of complete dewetting in Figure 3-4 is a result of slower dewetting because hydrophobicity needs to move the liquid against opposing capillarity. Although these findings are helpful to find good conditions of dewetting, it is hard to estimate a real Hamaker constant of the system. Also experimental confirmation of the theory is left behind. These are future subject of this study.

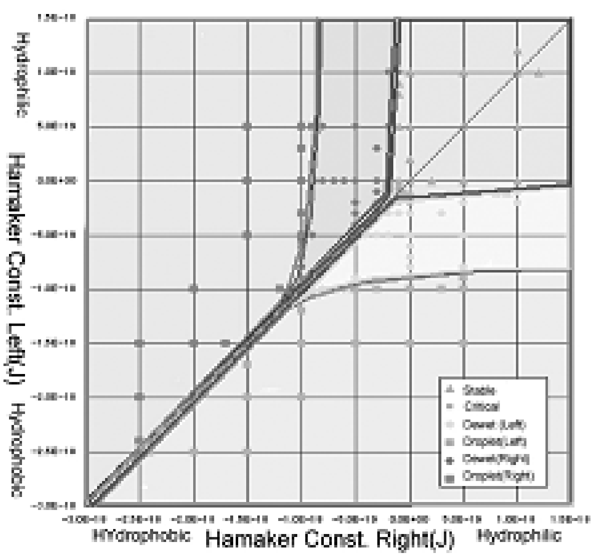

Fig. 3-3 Combination of Hamaker const. on Flat surface

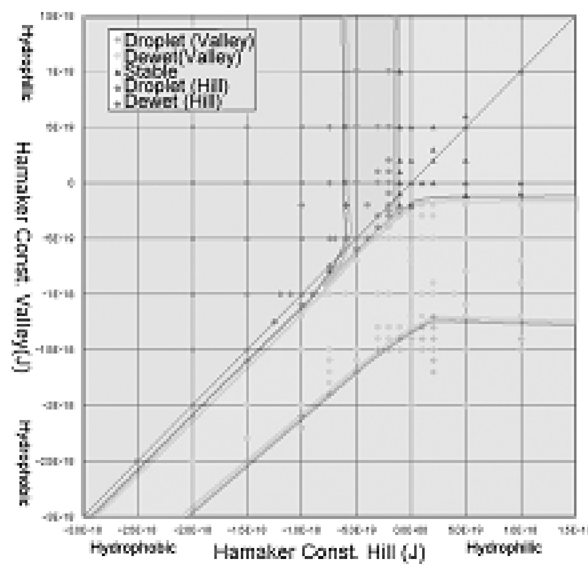

Fig.3-4 Combination of Hamaker const. on Wavy surface

Literatures

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