# Effect of Pd Additive on Ni-MILC Behavior

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It is known that Pd shows a lower crystallization temperature and a faster metal-induced lateral crystallization rate than Ni. However, Pd-MILC cannot be used for the fabrication of thin film transistors (TFTs), due to its unacceptable crystal quality. In this study, a mixture of Pd and Ni was used as a catalyst in MILC in an attempt to obtain high-quality poly crystals with an enhanced crystallization rate at a low crystallization temperature. The effect of the amount of Pd additive on the Ni-MILC behavior was systematically investigated. It was found that optimal TFT performance could be obtained when 5% by volume of Pd is added to a Ni catalyst. The On/Off ratio and electrical mobility were observed to be 10<sup>-6</sup> and more than 20 cm<sup>2</sup>/Vs, respectively, which are quite acceptable for practical use.

Keywords: LTPS, MILC, active matrix, TFT, metal catalyst

#### **1. INTRODUCTION**

Poly Si thin film transistors (TFTs) have drawn a considerable interest among researchers, because they are essential for fabricating the built-in driving circuitry in active-matrix liquid crystal display (AMLCD) devices. Poly Si TFTs show much higher electron mobility than a-Si TFTs do, enabling all three vital display factors-brightness, resolution, and image transport speed-to be improved. A heat treatment temperature of higher than 650 °C is, however, required for a-Si to be transformed into poly silicon, and common glass substrates cannot bear such high temperatures. Hence, either a quartz substrate, which is cost prohibitive for use in most display devices, or a low-temperature poly silicon (LTPS) technique should be used to fabricate poly silicon TFTs<sup>[1-5]</sup>. Typical examples of LTPS techniques are eximer laser annealing (ELA)<sup>[1]</sup>, metal-induced crystallization (MIC)<sup>[2]</sup>, rapid thermal annealing  $(RTA)^{[3]}$ , and metal-induced lateral crystallization (MILC)<sup>[5,6]</sup>. Poly silicon crystallized by ELA demonstrates good crystal quality, but the inevitable scan overlap results in non-uniform crystal quality, and the surface roughness caused by the liquid-solid phase transformation requires a chemo-mechanical polishing (CMP) process, which is significant production step. With MIC, it is possible to obtain poly crystalline film at an annealing temperature of below 500 °C. The MIC TFT, however, suffers from metal contamination, which causes unacceptably high leakage current<sup>[2,7]</sup>. Another method, RTA, incurs thermal shock problems, such as a low voltage breakdown of the gate oxide, glass bending, and uniformity.

Metal-induced lateral crystallization was discovered and termed by S.K. Joo in 1995<sup>[6]</sup>. By this technique, LTPS and an amorphous silicon thin film can be crystallized into poly silicon at temperatures below 600 °C, which is normally too low for such phase transformation. Thus far, only Pd and Ni have been shown to induce the MILC phenomenon<sup>[5,6]</sup> and the basic mechanism underlying MILC is not yet understood. Unlike MIC, no metal contamination is observed in the resulting crystallized area with MILC<sup>[6,9]</sup>. Therefore, a MILC TFT shows low leakage current and high electrical mobility, enabling its application to AMLCD and AMOLED<sup>[8]</sup>. The Pd-MILC process shows rapid crystallization at relatively low temperatures, but it results in many needle shaped grains containing numerous micro twin defects, causing the electrical performance of Pd-MILC TFTs to be unacceptable for LCD and/or OLED applications<sup>[9]</sup>. Alternatively, Ni-MILC occurs at a relatively slow rate; however, the resulting crystal quality is sufficient for poly TFT fabrication<sup>[1,10]</sup>.

In this work, a mixture of Pd and Ni was used as a metal catalyst in MILC in an attempt to obtain high-quality poly crystalline silicon film at a relatively high crystallization rate. The MILC behavior upon Pd addition was investigated, and Ni-MILC TFTs with differing amounts of Pd addition were fabricated. The effect of Pd additive on the electrical performance of Ni-MILC TFTs was analyzed to determine the optimal amount of Pd additive for TFT fabrication.

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# 2. EXPERIMENTAL

Four-inch Corning 1737 rectangular glass was used as a substrate. A 3000-Å buffer-oxide layer was formed on the glass substrate by PECVD, and a 600-Å a-Si thin film was deposited by LPCVD. Then, the active area was defined. The gate oxide and the gate metal were deposited sequentially, followed by the gate definition. Afterwards, Ni and Pd were sputter deposited for MILC and PR stripped to be put into furnace at 550 °C, hydrogen ambient. The MILC length was examined with an optical microscope. Other processes were carried out according to the common processes for TFT fabrication in a class 100 environment. Thus, each fabricated PMOS TFT was analyzed at a 4-point probe station.

## **3. RESULTS AND DISCUSSION**

Figures 1(a) and 1(b) show Nomarski optical micrographs after the two-hour, 550 °C heat treatment in a hydrogen ambient. The boundary between the crystallized and amorphous areas can be distinguished clearly in these optical micrographs. In addition, SEM shows that Pd-MILC produces needle shape crystals, while Ni-MILC produces flat shape crystals. When a mixture of these two metals is used for MILC, the resulting crystal is flat and similar to that of the Ni-MILC process.

With Pd-MILC, there is a spacing effect such that the MILC rate becomes higher as the metal line spacing becomes closer, and no appreciable lateral growth can be observed in an island type pattern. This phenomenon, the so-called spacing effect, is not observed with the Ni-MILC process. In Fig. 2, the spacing effect is shown in a mixed metal MILC. It is obvious in the case of Pd that as the spacing decreases, faster the lateral growth so that the maximum we can observe as the MILC rate is 7 m/hr at 550 °C when the spacing becomes less 50 m. When the spacing becomes larger than around 250 m, the spacing effect ceases, and no



Fig. 1. Optical micrographs after 550 °C, 2 hr heat treatment.
(a) The distance between the metals are 58 μm
(b) The distance between the metals are 102 μm

appreciable grow can be observed. The mixture MILC shows a spacing effect similar to that of Pd-MILC. It is interesting to notice the existence of the spacing effect in the mixture MILC, even though the resulting crystalline is not needle-shaped, but is rather flat and similar to that of Ni-MILC.

Figure 3 shows the effect of Pd addition on the spacing effect in Ni-MILC. It can be seen that the MILC rate becomes faster as the amount of Pd additive increases. In addition, the effect of Pd addition on the MILC rate becomes more considerable as the spacing of the metal catalysts decreases. The critical spacing, where the spacing effect first appears, tends to be larger as the amount of Pd additive increases.

Figure 4 shows that the MILC rate increases as the amount of Pd additive increases. In this experiment, the space distance was fixed at 44 m. It is interesting to notice that even a small concentration of Pd additive, even 1%, enhances the



Fig. 2. MILC growth length vs. the distance between the metal catalysts All samples were annealed at  $550 \,^{\circ}$ C for 2 hrs in a hydrogen ambient.



Fig. 3. Comparison of the spacing effect among various Pd concentrations in Ni-MILC All samples were annealed at 550 °C for 2 hrs in a hydrogen ambient.



Fig. 4. Relationship between the amount of Pd additive and the MILC rate All samples were annealed at 550 °C for 2 hrs in a hydrogen ambient.



Fig. 5. Variation of the MILC rate with respect to the Pd concentration at various spacings. All samples were annealed at 550 °C for 2 hrs in a hydrogen ambient.

MILC rate considerably. Research concerning the basic reaction mechanism for that is underway.

It can be seen in Fig. 5 that the MILC rate increases and then decreases with an increase of the amount of Pd additive, regardless of the spacing distance. With up to 50% of Pd addition, the MILC rate increases; however, beyond 50%, the MILC rate decreases in all cases. It may be reasonable to say that up to 50% of Pd concentration, the mixture catalysts act as Ni; however, when the amount of Pd is more than 50% in the mixture catalyst, it works as Pd. The experimental results indicate that a small amount of Ni enhances the Pd-MILC rate and that a small amount of Ni enhances the Pd-MILC significantly. It should be noticed that at this spacing, the Pd-MILC rate is very low, as shown in Fig. 5.

Three different methods were used to prepare the mixed metal catalyst: Ni on Pd, Pd on Ni, and co-sputtering Pd and Ni. As can be seen in Fig. 6, there is no significant difference



Fig. 6. Effect of the metal layer deposition method on the MILC rate. Total thickness was fixed as 200 Å. All samples were annealed at  $550 \,^{\circ}$ C for 2 hrs in a hydrogen ambient.



Fig. 7. I-V curves of 5% Pd-added Ni-MILC TFT (PMOS).

in the MILC rates from among these mixture preparation methods. However, as seen in Fig. 6, significant enhancement in the MILC rate is achieved by using 50 : 50 mixtures of Pd and Ni, as compared with pure Pd or Ni-MILC. Figure 6 also shows the spacing effect in Pd-MILC, while no such effect appears in Ni-MILC.

Figure 7 shows the electrical characteristics of the Ni-MILC TFT where 5% by volume of Pd was added to Ni. The slope, mobility, and On/Off ratio are about 1, 20, and  $10^{-6}$ , respectively. These parameters are not the best, but they are acceptable for most LCD applications. It should be noticed that a small amount of Pd addition, such as 5% is sufficient to enhance the MILC rate without sacrificing the electrical performance significantly. This observation strongly indicates that further lowering of the crystallization temperature is possible by improving the catalyst in MILC.

#### 4. CONCLUSION

Pd was added to Ni during Ni-MILC, and the effect of the additive amount on the MILC behavior has been systematically investigated. Generally, no spacing effect is observed during Ni-MILC; however, even a small amount of Pd additive during Ni-MILC brought about the spacing effect. The optimal concentration of Pd additive to achieve the maximum MILC rate was observed to be around 50 percent by volume. The critical spacing distance increases as the amount of Pd additive increases. The best electrical performance can be obtained when 5% of Pd is added to Ni-MILC. It turns out that the electrical parameters of the thus-fabricated TFT are not the best, but they are acceptable for most AMLCD applications. The fact that significant enhancement in the MILC rate can be achieved by the addition of a small amount of Pd to Ni during Ni-MILC indicates that even further lowering of the crystallization temperature is possible by manipulation of the metal catalysts, such as mixing, sequential deposition, and various heat treatment methods.

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