# 奈米級銅製程技術及高分子生醫微 流體晶片之研究

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#### 摘 要

隨著超大型積體電路線寬降低,電遲滯效應(RC delay)將愈來愈嚴重,而在線寬 $<0.13\mu m$  時,則鋁導線製程,將被銅導線製程取代。因為:(1)銅具有比鋁更低的電阻率 $(\rho_{Cu(20^{\circ})}=1.67\mu\Omega$ -cm;  $\rho_{AI(20^{\circ})}=2.66\mu\Omega$ -cm);(2) 在高電流密度  $(10^{9}A/cm^{2})$ 下,抗電子遷移能力比鋁高了四個量級數(order);(3)良好的抗應力導致的空洞形成性質等等優點。

採用銅的製程雖然可以克服鋁金屬製程的優點,但銅很容易擴散到矽裡面去,會影響到效能,此外銅和鋁一樣會與矽作用而導致銅金屬穿透電晶體的接面造成短路;同時銅在矽晶體中是一種 deep-level 的摻質(dopant),即使不短路也會影響少數載體(minor carrier)的壽命(lifetime),而增加接面(junction)的漏電流(leakage current)。為了防止銅到達矽的區域破壞元件,銅導線與栓塞(plug)必須在所有的方向與層次完全的封住。所以必須在銅與矽的界面上,增加一層用來隔離它們兩者的擴散阻障層(diffusion barrier),以阻止銅與矽的反應。且銅的低揮發特性使其無法像 Al 製程般可蝕刻成型,而隨著銅化學機械研磨技術的開發使得銅導線技術被實現了。然而因為銅的材料特性使得研磨產生了許多的缺陷及微

刮痕(defect and microscratch)如此將大大的降低良率。

生物晶片(biochip)是運用分子生物學、基因資訊、分析化學等原理進行設計,以矽晶片、玻璃或高分子為基材,配合微機電、自動化或其他精密加工技術,所製作之高科技元件。有如半導體晶片能快速進行繁複運算;生物晶片具有快速、精確、低成本之生化分析檢驗能力。生物晶片應用領域涵蓋生命科學基礎研究、新藥研發、醫療診斷、食品安全、化工生產等,極具潛力。然而生化檢體成分複雜不易達成檢體處理自動化。

本論文將焦點放在奈米級銅製程技術及高分子生醫微流體晶片兩部分研究上:

(1) 為了獲得高效能銅擴散阻障層,我們使用  $NH_3/Ar$  或  $N_2/Ar$  之混合氣體 在矽基材上用反應性射頻濺鍍(reactive RF sputtering)成長  $TaN_X$  擴散阻障層薄膜,並比較其奈米特性。我們量測經過快速熱處理之  $Cu/TaN_X/n^+np^+$ 二極體的漏電流(leakage current)用來判斷  $TaN_X$  擴散阻障層的熱穩定性。 $TaN_X$  薄膜其熱穩定性和結構較有關,和反應氣體種類較無關。較高 N/Ta 可使整個  $Cu/TaN_X/n^+np^+$ 二極體結構熱穩定性較佳,但 N/Ta 太高將使得電阻係數過高,所以當 N/Ta 約等於 1 時為一熱穩定性好,電阻係數適中之比例。

為了選擇適當特性的銅化學機械研磨液,我們使用紅外線熱影像儀來分辨 此研磨液是屬於普勒斯頓(Preston)或非普勒斯頓(non-Preston)。採用紅外線熱影 像儀即時選擇合適的非普勒斯頓銅化學機械研磨液並找到最佳的各步驟製程切 換點。再加上穩健的化學機械研磨機和適當的銅膜性質及前處理,我們可以獲得 一總缺陷數少於  $10^1$  並達到優秀銅化學機械研磨結果。如此的銅化學機械研磨技 術使得銅鑲埋製程可行更讓  $0.13~\mu m$  或 100~n m 以下的銅製程可靠的被實現。 (2) 本研究將核酸萃取微粒固定於檢體前處理晶片中改善下述四點: 加速檢體處理程序、減少檢體使用量、簡化檢體處理及達到檢體處理自動化。當核酸萃取微粒未固定於檢體前處理晶片中,只是簡單混入生化溶液大分子易遮蔽核酸與微粒官能基結合既使溶液來回流動。當核酸萃取微粒固定於檢體前處理晶片中,所有試劑的碰撞頻率將增加,如此將增加萃取效率。使用高分子溶液可固定核酸萃取微粒於基材表面,但是使用電漿處理晶片基材更可改變活化其表面,如此核酸萃取微粒將能與基材表面形成共價鍵結進而改善核酸萃取效率。



Studies on the Nano-Scale Cu Process

Technology and Polymeric Microfluidic

**Biochip** 

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**ABSTRACT** 

As the line width of ULSI (Ultra-Large Semiconductor Integration) decreases,

the related RC delay problem becomes more serious. Aluminum will be replaced by

copper when the line width is smaller than 0.13µm because copper possesses better

conductivity and lower electro-migration. However, Cu tends to diffuse into Si and

affects its device performance. Cu diffusing into Si transistors leads to deep-level

doping that will result in lower life timer of minor carrier and higher junction leakage

current. In order to prevent Cu diffusing into Si and avoid device damage, a barrier

layer between Si and Cu is required. In addition, Cu is more difficult to be etched by

plasma due to its lower volatility relative to Al. Since the Cu CMP process has been

developed, the copper damascene process has become feasible. However, CMP

process tends to create defects such as microscrat, dishing, erosion and thus

significantly reduces product yield.

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Biochip technology combines biomolecular science, Gene information and analytic chemistry using the substrate materials of silicones, glasses or polymers. MEMS, automation and other fine fabrication technologies are adopted to manufacture this high technology device. Similar to semiconductor possessing capability of rapid and complex computation, biochips can also conduct fast, accurate and low cost bio-analytic capability. Biochips have potential applications in the fundamental research in life sciences, the development of new drugs, clinical disease diagnosis, food security, chemical industry and other areas. However, it is rather difficult to perform automatic sample-preparation due to the complexity of biochemical samples.

In this thesis, we focus on areas of the nano scale Cu process technology and the polymeric microfluidic:

(1) To obtain high efficient Cu diffusion barriers, nanoscale  $TaN_X$  diffusion barrier thin films were prepared by RF reactive sputtering with NH<sub>3</sub>/Ar and N<sub>2</sub>/Ar as reactive gas mixtures. After rapid thermal annealing, the leakage currents of  $Cu/TaN_X/n^+np^+$  diodes were measured that allowed us to determine the thermal stabilities of the  $TaN_X$  diffusion barriers. The thermal stabilities of the  $TaN_X$  films predominantly depend on their crystal structures, and less on the gas source. Higher N/Ta ratio results in improved thermal stability of the  $Cu/TaN_X/n^+np^+$  diode structures but higher resistivity if this ratio becomes too high. When the N/Ta ratio is ca. 1, the films exhibits good thermal stability and moderate resistivity.

In order to choose appropriate Cu CMP (Chemical-Mechanical Polishing) slurry, an in-situ IR thermal camera is employed to distinguish this slurry Preston or non-Preston type. The adoption of the IR thermal camera is to choose suitable non-Preston Cu CMP slurry in-situ and to optimize changing timing of step endpoint.

Combination of robust CMP machine, appropriate Cu film quality and pretreatment, we can achieve excellent Cu CMP performance with total defect number less than 10<sup>1</sup> order. Such an improved Cu CMP technology makes the Cu damascene process workable and process of prepare Cu, 0.13 µm and beyond 100 nm, becomes reliable and practical.

(2) In this study, DNA extraction beads fixed on the sample-preparation chip result in following improvements: acceleration of sample-preparation procedure, minimization of required sample quantity, simplification of sample-preparation, and complete automation of the process.

If the DNA extraction beads are not fixed on the sample-preparation chip simply by mixing with biochemical solution, these macromolecules tend to hinder the combination of DNA with functional group of these beads, even with liquid flows back-and-forth. When these DNA extraction beads are fixed on the sample-preparation chip, the contact rate of both reactants increases and results in higher extraction efficiency. A thin micro layer of polymer solution is able to fix the DNA extraction beads on the substrate surface. In addition, plasma treatment of the chip substrate can change and activate its surface. Thus, these DNA extraction beads can be bonded covalently with the substrate surface and further improve its efficiency of DNA extraction.

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| wt% PMMA/EA-MeOH, (d) 20.0 wt% PMMA/EA-MeOH.                                 | 86 |

| inside              | sample preparation chip with different concentration                  | 1  |
|---------------------|-----------------------------------------------------------------------|----|
| PMMA                | VEA-MeOH on PMMA substrate. Lane (1) ~ (2) were                       | 2  |
| positive            | e control; Lane (3) was 5.0 wt% PMMA/EA-MeOH; Lane                    | 9  |
| (4) was             | s 10.0 wt% PMMA/EA-MeOH; Lane (5) was 15.0 wt%                        |    |
| PMMA                | VEA-MeOH; Lane (6) was 20.0 wt% PMMA/EA-MeOH.                         | 87 |
| Figure 4-7: Optical | l microscope images - Dispersing solutions of different               | t  |
| concent             | tration on PC substrates (a) 5.0 wt% PMMA/THF-MeOH                    | •  |
| (b) 1               | 10.0 wt% PMMA/THF-MeOH, (c) 15.0 wt%                                  | )  |
| PMMA                | /THF-MeOH, (d) 20.0 wt% PMMA/THF-MeOH.                                | 88 |
| Figure 4-8: Agaros  | se gel electrophoresis diagram of DNA extraction beads                | S  |
| inside              | sample-preparation chip with different concentration                  | 1  |
| PMMA                | THF-MeOH on PC substrate. Lane (1) was 5.0 wt%                        | )  |
| PMMA                | THF-MeOH; Lane (2) was 10.0 wt% PMMA/THF-MeOH                         | ;  |
| Lane (              | (3) was 15.0 wt% PMMA/THF-MeOH; Lane (6) was                          | S  |
| positive            | e control.                                                            | 89 |
| Figure 4-9: Compar  | rison of agarose gel electrophoresis diagram of fixed DNA             | 1  |
| extracti            | on beads under $NH_3 + O_2$ plasma surface treatment and free         | 3  |
| beads. I            | Lane (1) was free beads (50 ng E. coli cells), Lane (2) was           | S  |
| free be             | eads (100 ng E. coli cells), Lane (3) was beads inside                | 3  |
| sample-             | -preparation chip pre using wash, Lane (4) was collecting             | 3  |
| beads i             | inside sample-preparation chip wash, Lane (5) was beads               | S  |
| inside s            | sample-preparation chip elution (100 ng E. coli cells), Land          | 3  |
| (6) was             | positive control.                                                     | 90 |
| Figure 4-10: Comp   | parison of Agilent 2100 bioanalyzer analysis diagram and              | 1  |
| data of             | fixed on DNA extraction beads (100 ng E. coli cells) under            | r  |
| $NH_3 + 0$          | O <sub>2</sub> plasma surface treatment and free beads (100 ng E. col | i  |
| cells).             |                                                                       | 91 |
|                     |                                                                       |    |
|                     |                                                                       |    |

Figure 4-6: Agarose gel electrophoresis diagram of DNA extraction beads