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碩士論文

利用矽鍺氧與矽鍺氮薄膜形成鍺奈米點
在非揮發性記憶體應用之研究

**Study on Formation of Ge Nanocrystal using SiGeO
and SiGeN layer for Nonvolatile Memory Applications**

研究 生：謝彥廷

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Advisor : Dr. Chun-Yen Chang



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利用矽鍺氧與矽鍺氮薄膜形成鍺奈米點 在非揮發性記憶體應用之研究

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摘要

近年來，可攜帶式電子產品被廣泛的使用，諸如數位像機、筆記型電腦、手機等等的產品，在市場上佔有重要的地位。而這些產品都需要運用到非揮發性記憶體(NVM)作為儲存資料中心，而非揮發性記憶體目前在元件尺寸持續的微縮下，其需求為高密度記憶單元、低功率損耗、快速讀寫操作以及良好的可靠度(Reliability)。然而傳統浮動閘極(floating gate)記憶體在操作過程中，穿遂氧化層產生漏電路徑會造成所有儲存電荷流失回到矽基版，隨著尺寸微縮這種情況會更糟，所以在資料保存時間(Retention)和耐操度(Endurance)的考量下，微縮穿遂氧化層的厚度是非常困難的。非揮發性奈米點記憶體及 SONOS 記憶體被提出希望可取代傳統浮動閘極記憶體，由於彼此分離的儲存點作為儲存中心，所以上述兩者可以有效改善小尺寸記憶體元件多次操作下的資料儲存能力。

在本文中，我們提出一種矽鍺氧(SiGeO)的堆疊結構作為作為鍺奈米點(Ge nanocrystal)的自我析出層(self-assembled layer)，並應用在奈米點非揮發性記憶體上。在室溫下，在氬氣及氧氣(Ar/O₂)的環境中濺鍍(sputtering)矽鍺(Si_xGe_{1-x})混合靶材，此方式可以成功的將氧摻入至矽鍺中形成矽鍺氧三元薄膜，另外，在我們的實

驗中，在熱退火之前先疊加上一層氧化矽為一個關鍵的步驟。之後我們再利用矽與鋯不同的氧化現象，經由快速熱退火製成來形成均勻且高密度($\sim 10^{12} \text{cm}^{-2}$)的鋯奈米點。並且我們延長熱處理的時間可以有效的分離鋯奈米點且減少奈米點周圍氧化矽及氧化矽中的缺陷(defects)，有效的降低電荷流失機率，改善資料保存時間。

同樣地，我們用相同的方式，在濺鍍的過程中將氧氣置換成氮氣，利用同樣的方式製作鋯奈米點且被包覆在氮化矽(SiN_x)的結構，其記憶效應比先前的鋯奈米點埋在氧化矽(SiO_x)結構還顯著，此乃因為鋯奈米點埋在氮化矽為主的載子儲存層中，會產生額外的儲存中心，進而增加記憶體效能，另外，我們也延長熱處理的時間，同樣低可以改善鋯奈米點間的隔離情況得到較大的記憶窗口，且改善資料保存時間。

另外，我們也嘗試利用高介電常數介電質(ErSiGeO)當作我們的電荷儲存層，可以有效的增加記憶體效應，且改善寫入讀取速度。以上這些應用在非揮發性記憶體的製成技術同時也適用於現階段積體電路製程。

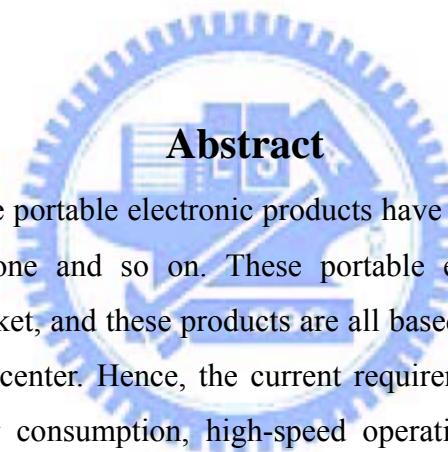


Study on Formation of Ge Nanocrystal using SiGeO and SiGeN layer for Nonvolatile Memory Applications

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Abstract

In recent years, the portable electronic products have widely applied, such as digit camera, laptop, cell phone and so on. These portable electronic products play an important role in the market, and these products are all based on the nonvolatile memory (NVM) for data storage center. Hence, the current requirements of NVM are the high density cells, low-power consumption, high-speed operation and good reliability for scaling down devices. However, all of the charges stored in the conventional floating gate NVM will leak back to substrate because the tunnel oxides have leakage paths during operation processes. It is even worse when being scaled down. Therefore, the thickness of tunnel oxide is difficult to scale down in terms of charge retention and endurance characteristics. The nonvolatile nanocrystal memory and SONOS memory are promising candidates to replace the conventional floating gate memory, because the discrete storage nodes of themselves are enveloped. Both of them are capable to improve data retention under operation and have been provided by the endurance test which is good for device further down scaling efficiently.

In this thesis, we proposed a SiGeO stacking structure serving as Ge nanocrystals self-assembled layer for application of nanocrystal NVM. We successfully incorporated oxygen into SiGe layer to form SiGeO ternary film by sputtering commixed $\text{Si}_x\text{Ge}_{1-x}$

target in an Ar/O₂ ambiance at room temperature. In addition we found out that pre-annealing-capping oxide (PACO) is a critical step in our experimental process, and then we used the different oxidized mechanism between Si and Ge. The uniform and high density ($\sim 10^{12}\text{cm}^{-2}$) of Ge nanocrystals was fabricated after a rapid thermal annealing (RTA) process. The Ge nanocrystals were isolated better and the defects (leakage path) in the SiO_x which surrounds the nanocrystal were reduced by increasing the thermal treatment time. This process can reduce the probability of charges losing and improve the data retention time.

As the same, we used similar method that oxygen was replaced by nitrogen. The Ge nanocrystals embedded in SiN_x structure was fabricated by using the same process. The memory window for the stacked structure with Ge NCs embedded in SiN_x layer is larger than Ge NCs embedded in SiO_x layer, due to the extra charge trapping centers generated for Ge NCs embedded SiN_x layer. Furthermore, we also increased the time for thermal treatment resulting in better Ge NCs isolation and less defects in the SiN_x. That improves the data retention time, too.

In addition, by using high dielectric constant layer (ErSiGeO) for charging tapping layer structure has better memory ability and the operation speed is improved, too. Finally, all of the above fabrication techniques for the application of nonvolatile nanocrystal memory can be compatible with current manufacture process of the integrated circuit manufacture.

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隨著本篇論文即將撰寫完成的同時，也代表著學生生涯即將告一段落，回想起這些年的來的求學階段，酸甜苦澀一點一滴彷彿時光倒流地浮現在我的腦海裡，能順利完成這個學位，要感謝的人很多，感激之情無以言表，但在我心中對你們總是抱著無限的感激。

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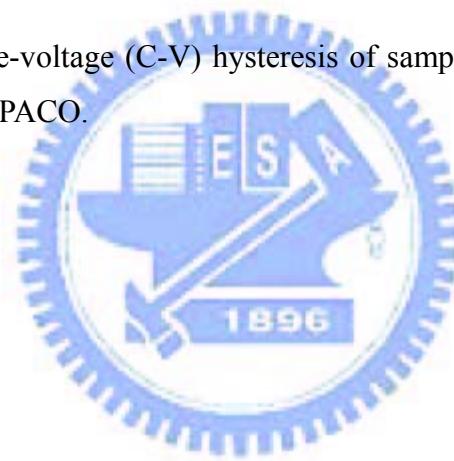
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Chapter 1

Introduction

1.1 General Background of Nonvolatile Memory

In recent years, the portable electronic products have widely applied in our life. Such as cellular phone, digital camera, laptop, PDA, memory cards, MP3 audio player, USB flash personal disk etc. These products are all based on flash memory which is nonvolatile and they can keep stored information when the power supply switches off. Flash memory also has several advantages, such as the ability to be electrical programmed and fast simultaneous block electrical erase in a single-cell, smaller cell size to achieve higher chip density, and better flexibility [1.1-1.2]. The flash memory fabrication process can be compatible with the current CMOS process and be a suitable solution for embedded memory application. Flash memories are easily scale down and replacement for EPROMs (Erasable Programmable Read Only Memory) and EEPROMs (Electrically Erasable Programmable Read Only Memory). As these critical advantages flash memory possesses, it has become the mainstream nonvolatile memory device in last few decades.

In 1960's, due to the high cost, large volume and high power consumption of the magnetic-core memory, the electronic industries urgently required a new kind of memory to replace the magnetic-core memory. In 1967, D. Kahng and S. M. Sze invented a new structure called floating-gate (FG) nonvolatile semiconductor memory at Bell Labs [1.3]. A standard conventional floating-gate device structure is shown in Figure 1-1. The structure is basic on a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) with a modified stacking gate which composed by control gate, dielectric, floating gate and dielectric as a sandwich structure. Silicon dioxide (SiO_2) is the most common dielectric which the FG was embedded in. The FG acts as a charge storage node. Charges injected into the FG were retained there, resulting in the threshold voltage shift of the cell transistor for nonvolatile application.

Nowadays, nonvolatile memory device are moving toward higher density memory array, lower power consumption, low cost, higher speed operation and better reliability. Therefore the flash memory devices come to be in face of their limitations. Although the

conventional FG memory does not need refreshing, consume less power and achieve higher array density. However, the FG memory has slower operation speed and poor reliability. In order to improve the program / erase speed of the FG memory, the thickness of tunnel oxide must be reduced. The tunnel oxide must be thin enough to achieve fast and efficient charge transport ability. On the contrary, tunnel oxide needs to provide superior isolation under retention, endurance and disturbed conditions to keep the data integrity to 10 years. When the tunnel oxide becomes thinner, program speed will be faster. But if we need better isolation and reliability, we should increase the thickness of the tunnel oxide. So that is a trade-off between the operation speed and the reliability. Currently, the tunnel oxide of the commercial flash memory devices is about 8-11nm, Resulting in high programming voltage and slow programming speed [1.4].

For the conventional FG memory, if there are several defects in the tunnel oxide after programming or erasing operated steps, might induce a leakage path. That make all charge stored in the FG leak back to the channel. That is why the conventional FG memory always needs thicker tunnel oxide to get better retention. In order to overcome the scaling limitations of the conventional FG structure, there are two most mentioned candidates. One is the semiconductor/oxide/nitride/oxide/semiconductor (SONOS) [1.5-1.7] nonvolatile memory device. The other one is nanocrystal [1.8-1.10] nonvolatile memory device. These two structures have been demonstrated to improve the retention time compared to the conventional FG memory. Therefore, the tunnel oxide thickness could be decreased for faster operation speed and lower operation voltages.

1.2 SONOS Nonvolatile Memory Device

Poly silicon/control oxide/silicon nitride/tunnel oxide (SONOS) nonvolatile memory device structure is shown in Figure 1-2. The charge storage elements in SONOS memory are the charge traps distributed throughout the volume of the silicon nitride layer. It is well known that silicon nitride contain a lot of traps, and the trap density is about 10^{18} - 10^{19} cm $^{-3}$ according to Yang et al [1.11] and stores both electrons and holes (positive charges) injected from the channel. The first nitride-base devices is metal-gate nitride device MNOS (Metal/Nitride/Oxide/Silicon) which was reported in 1967 by Wegener et al [1.12]. Figure 1-3 illustrates the progression by the device cross section, which has led to the SONOS device structure. Initial device structures in the early 1970s were p-channel metal/nitride/oxide/silicon (MNOS) structure with aluminum gate electrodes and 45nm thick silicon nitride charge storage layers. Write/erase voltages were typically

25-30 V. In the late 1970s and early 1980s, scaling moved to n-channel SNOS devices with program / erase voltages of 14-18 V. In the late 1980s and early 1990s, n- and p-channel SONOS devices emerged with program / erase voltages of 5-12 V. In the SONOS device, an oxide layer is introduced between the gate and the silicon nitride region. Thus, it forms the ONO ($\text{SiO}_2/\text{Si}_3\text{N}_4/\text{SiO}_2$) gate dielectric stack (Fig. 1-2) instead the nitride layer with just a metal or semiconductor gate. The purpose of top blocking oxide is to reduce the charge injection from the control gate into nitride layer, limiting the memory window of both MNOS and SNOS devices.

The SONOS memory devices have attracted a lot of attention due to theirs several advantage over the conventional FG flash memory devices. Include reducing process complexity, getting higher operation speed, lowering operation voltage, improving endurance and elimination of drain-induced turn-on [1.13-1.15]. The main difference between the conventional FG flash and SONOS memory is the charging method. Conventional FG structure charges carrier in the continuous conductive polysilicon. On the other hand, SONOS structure charge carrier in the physical discrete traps of the silicon nitride dielectric. The charge stored in the silicon nitride can not move easily, hence the SONOS can bear the defect in the tunnel oxide induced the leakage path. Therefore, the SONOS memory device has better endurance the conventional FG memory.

The SONOS memory device still has to face the challenge in the future for high density nonvolatile memory application, which require lower power ($< 5\text{V}$), lower power consumption, faster operation speed, longer retention time and superior endurance characteristics. A lot of approaches have been proposed for improving the SONOS performance and reliability. Chen *et al.* demonstrated a Si_3N_4 bandgap engineering (BE) control method for better endurance and retention. A nitride with varied relative Si/N ratio throughout the film has increased the charge-trapping efficiency significantly [1.16]. She *et al.* demonstrates that high-quality nitride is applied as the tunnel dielectric for a SONOS-type memory device. Compared to control devices with SiO_2 tunnel dielectric, faster programming speed and better retention time are achieved with low programming voltage [1.17]. Chen *et al.* studies a polycrystalline silicon thin-film transistor (poly-Si TFT) with oxide/nitride/oxide (ONO) stack gate dielectrics and multiple nanowire channels for the applications of both nonvolatile silicon-oxide-nitride-oxide-silicon (SONOS) memory and switch transistor [1.18]. The proposed NW SONOS-TFT exhibits

superior memory device characteristics with high program/erase efficiency and stable retention characteristics at high temperature. Such a SONOS-TFT is thereby highly promising for application in the future system-on-panel display applications.

In recent research, high-k dielectric materials were proposed to replace the silicon nitride film as trapping layer, such as HfAlO and Al₂O₃ [1.19]. HfAlO with 10% Al₂O₃ has very similar band offset to pure HfO₂. The conduction band offset of HfAlO with respect to Si is the smallest (1.63 eV), compared to 2 eV for Si₃N₄ and 2.8 eV for Al₂O₃. Hence, at the same gate bias where modified F-N tunneling dominates, the electron tunneling distance from the Si substrate to the conduction band of the storage dielectric layer is shortest in HfAlO and longest in Al₂O₃ [1.20]. The over-erase phenomenon in the SONOS memory structure is minimized by using hafnium oxide (SOHOS) to replace silicon nitride (SONOS) as the charge storage layer. Unlike SONOS devices, SOHOS structures show a reduced over-erase phenomenon and self-limiting charge storage behavior under both erase and program operation. These are attributed to the differences in band offset and the crystallinity of the charge storage layer [1.21].

1.3 Nanocrystal Nonvolatile Memory Device

Nanocrystal nonvolatile memories are one particular implementation of storing charge by dielectric surround nanodots, and were first introduced in the early 1990s by IBM researchers who proposed flash memory with a granular floating gate made from silicon nanocrystals [1.8]. The name nanocrystal referred to a crystalline structure with a nanoscale dimension. And its electric properties are more similar to an atom or molecule rather than the bulk crystal. Figure 1-4 shows the nanocrystal nonvolatile memory device structure. We can find out that the nanocrystals are separated with each other and embedded in the gate dielectric layer. In the nanocrystal nonvolatile memory device, the charges were charged in the isolated nanocrystals instead of the continuous FG polysilicon layer. Each nanodots will typically store only a handful of electrons; collectively the charges stored in these dots control the channel conductivity of the memory transistor.

Nanocrystal NVM devices have been attracted a lot of attentions recently due to the potential to overcome the limitations of traditional FG NVM. Using the nanocrystal to store charge offers several advantages. The main one is the potential to use thinner tunnel oxide without sacrificing nonvolatility. This is quite attractive issue since reducing the tunnel oxide thickness is a main factor to lowering operating voltages and/or increasing

operating speed. This claim of improved scalability results not only from the distributed nature of the charge storage, which makes the storage more robust and fault-tolerant, but also from the beneficial effect of Coulomb blockade [1.22]. And the lateral charge migration phenomenon will be suppressed by the mutually isolated nanocrystals with each other. Quantum confinement effects (bandgap widening; energy quantization) can be exploited in sufficiently small nanocrystal geometries (sub-3nm dot diameter) to further enhance the memory performance. There are other important advantages for nanocrystal NVM device. First, the fabrication of the nanocrystal memories is more simplified and lower process cost as compared to the conventional FG memories. Second, due to the absence of drain to FG coupling, nanocrystal memories suffer less drain induced barrier lowering (DIBL) and therefore have intrinsically better punch-through characteristics. This advantage is gained a higher drain bias during the read operation, thus improving memory access time [1.23]. It allows using shorter channel lengths and therefore smaller cell area. Third, nanocrystal memories are characterized by excellent immunity to stress induced leakage current (SILC) and oxide defects due to the distributed nature of the charge storage in the nanocrystal layer. The other is low capacitive coupling between the external control gate and the nanocrystal charge storage layer. This does not only result in lower operating voltages, thus offsetting the benefits of the thinner tunnel oxide, it also removes an important design parameter (the coupling ratio) typically used to optimize the performance and reliability tradeoff.

The fabrication of a nonvolatile memory cell requires a perfect control of four parameters: (1) the thickness of tunnel oxide, (2) the density of nanocrystals, (3) the size of nanocrystals, and (4) the thickness of control oxide. An important issue of the nanocrystals memory is the average dot size and the nanocrystal density. Larger dot size provide faster program / erase speed due to smaller quantum confinement and coulomb blockade effects and hence better carrier tunneling injection. But it also shows undesirable disadvantages with large size nanocrystal. Stress induced leakage during retention is one of them to make the device worse reliability. And as the nanocrystal size increase, the density of nanocrystal will be decrease. Thus it is also a trade-off between operating speed and reliability in selecting size of nanocrystal. A typical target is a density at least 10^{12}cm^{-2} , and requires nanocrystal size be about 5 nm and below. Moreover, good process control is needed with regards to such nanocrystal features as: planar nanocrystal layer; inter-crystal interaction (lateral isolation); and crystal doping (type and level). Finally, it is preferred that that the fabrication process is simple and that

it uses standard semiconductor equipment.

After S. Tiwari proposed silicon nanocrystal memory devices instead of FG memory. In order to improve the data retention by Coulomb blockade effect, double layer silicon nanocrystal memory has been invented [1.24]. It seems interesting to use Ge nanocrystals rather than Si nanocrystals because of its smaller band gap and higher dielectric constant. Indeed King and Hu have recently demonstrated the superior memory properties of Ge based nanocrystal memories over those based on Si [1.25]. As the size and size distribution of the nanocrystals have been considered, She *et al.* [1.26] made a conclusion on Ge nanocrystal memory device that size around 5 nm is preferred to achieve fast programming speed and longer retention time. And size should not be scale below 5 nm due to the quantum confinement effect will be very significant.

There are several nonocrystal fabrication processes which have been demonstrated. Numerous effort have focused on obtaining a high density of nanocrystals through a variety of techniques including aerosol technique, ion implantation, direct chemical vapor deposition (CVD), evaporation deposition such as sputter, dual E-gun, MBE and re-crystallization annealing of amorphous silicon (α -si). Kim *et al.* used conventional low pressure chemical vapor deposition (LPCVD) to fabricate silicon nonocrystals at 620 °C [1.27]. Direct CVD of silicon is preferred over ion implantation and re-crystallization annealing because it is difficult to control the required amount of silicon in the stack. Further, nucleation and growth by CVD provides simpler processing to control the size and the density of nanocrystals. Silicon nanocrystals with density between 10^{11} and 10^{12}cm^{-2} have been deposited in various dielectrics such as SiO_2 Si_3N_4 and Al_2O_3 by using CVD process. A higher density about $5\times10^{11}\text{cm}^{-2}$ was obtained on nitride surface, and the density was more than three times larger that on oxide surface[1.28]. Fernandes *et al.* acquired the higher Si quantum dots density ($\sim10^{12}\text{cm}^{-2}$) by integrating on $\text{SiO}_2/\text{Al}_2\text{O}_3$ tunneling dielectrics [1.29]. To fabricate Ge nanocrystals, the oxidation of mixed SiGe films has been proposed [1.25]. As the SiGe layer be oxidized, the Ge element will be segregated and Si will be oxidized into SiO_2 [1.30-1.31]. Ostraat *et al.* proposed an aerosol silicon nanocrystal nonvolatile memory device with large threshold voltage shift ($>3\text{V}$), sub-microsecond program times, millisecond erase times, excellent endurance ($>10^5$ program/erase cycles), and long term retention ($>10^6$ sec) [1.32].As for the tunnel dielectric for nanocrystal NVM devices, high- k tunnel dielectric were investigated [1.16] [1.28] [1.33]. Results show that due to its unique band asymmetry in

programming and retention mode. Using high- k dielectric on Si channel offers lower electron barrier height and larger dielectric thickness resulted in much higher $I_{G,\text{Write/Erase}}/I_{G,\text{Retention}}$ ratio than SiO_2 . Therefore, we get faster program / Erase speed and longer retention.

In the future, the primary drivers behind nanocrystal memories are the potential to reduce the tunnel oxide thickness, resulting in lower operating voltages, and the simplicity of a single poly-silicon process. But there are still challenges for nanocrystal memories in the long road to commercialization. Nanocrystal memories have yet to deliver on most of their promises. In reality, part of the voltage gain is offset because of the poor control gate coupling. For fabrication processes, it is hard to control the uniformity of the nanocrystal size and their physical locations in the channel. It is not a surprise that nanocrystal memories exhibit large device-to-device variation. Moreover, it has yet to be demonstrated that both the nominal and the statistical retention behavior are sufficient to meet true non-volatility requirements. Although single-dot memories have been demonstrated [1.34-1.35], but a more fundamental understanding of the scaling limits of nanocrystal memories is necessary, concentrating especially on the aspect of controlling channel conductance when relying on only a few discrete charge centers [1.36]. Finally, in order for that to happen, their claimed benefits will need to be more unambiguously substantiated, and a more appealing bundle of memory features will have to be demonstrated.

1.4 Motivation

For nonvolatile semiconductor memories is to achieve low power, low voltage performance. For nonvolatile flash memories, two limitation had encountered at the present time are: (1) The limited potential for continued scaling of device structure, The scaling limitation stems from the extreme requirements put on tunnel oxide layer. In order to get balance between program / erase speed and retention time, it is a trade-off to get the optimal tunnel oxide thickness. (2) The quality and strength of tunnel oxide after plenty of program / erase cycles. Once a leaky path has been created in tunnel oxide, all the charge stored in the floating gate will be lost. Therefore, two kinds of new structure was suggested, SONOS and nanocrystal NVM devices, are proposed to overcome this oxide quality limit of the conventional FG structure.

These technologies replace the FG structure with a great number of charge-storage nodes in the dielectric or in the nanocrystal. Unlike the FG, the local leakage path will not

cause the entire loss of information for the nanocrystal NVM device. This effectively prevents the leakage of all the stored charges out of the floating gate.

In this thesis, a new idea of crystallize nanocrystal was be proposed. We chose sputter system which is lower cost than furnace system. To deposited a SiGeO film by sputtering SiGe co-mix target in Ar/O₂ ambient to replace the FG in flash structure. This is a new process to deposit a ternary SiGeO compound. We also chose rapid thermal annealing (RTA) to reduce thermal budget than furnace annealing to avoid Ge over oxidizing. After thermal treatment, Ge in the SiGeO film will be segregated to form Ge nanodots embedded in the SiO_x dielectric. And it shows memory effect and reaches the requirement of retention of 10 years and reliability for NVM application. Furthermore , we proposed a other new ternary SiGeN compound. Using the similar process to form Ge nanodots embedded in SiN_x dielectric. And it also show memory effect and reaches the requirement for NVM application.

1.5 Organization of This Thesis

This dissertation is divided into six chapters. The contents in each chapters are described briefly as follows:

In chapter 1, general background of nonvolatile memory, conventional flash memory, SONOS nonvolatile memory and nanocrystal memory are introduced.

In chapter 2, basics of program and erase operation are introduced.

In chapter 3, the Ge nanocrystal embedded in SiO_x NVM structure, experimental process flow, results and discussions will be stated in this chapter.

In chapter 4, the Ge nanocrystal embedded in SiN_x NVM structure, experimental process flow, results and discussions will be stated in this chapter.

In chapter 5, the Ge doped in Erbium silicate high-*k* dielectric film, which is a SONOS type NVM structure, experimental process flow, results and discussions will be stated in this chapter.

In chapter 6, the final chapter is included the conclusions and the future work.

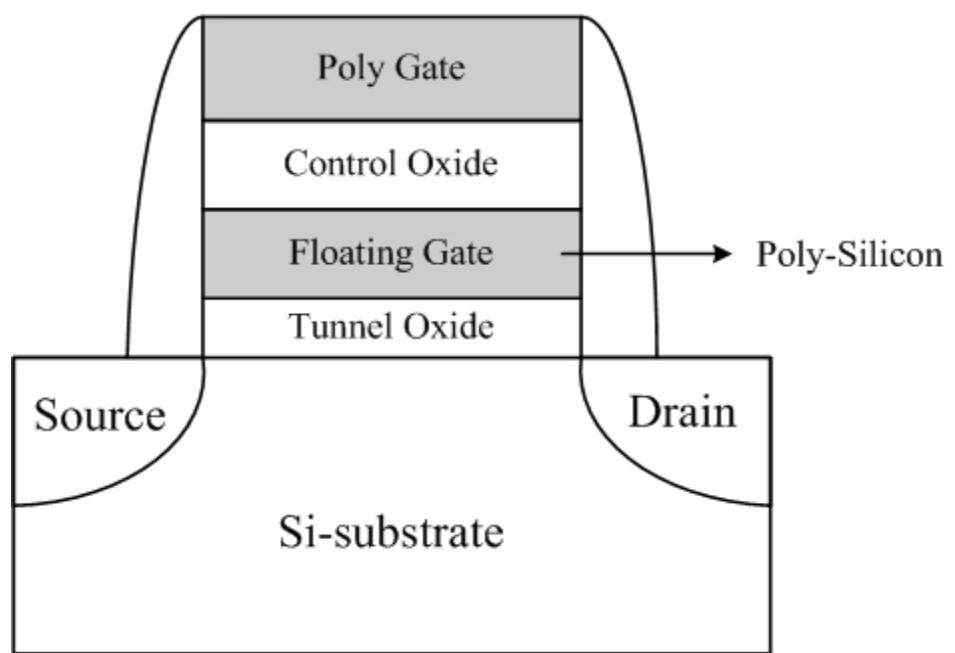


Figure 1-1 The structure of the conventional floating-gate (FG) nonvolatile memory device. Continuous poly-silicon gate is used as the charge storage element.

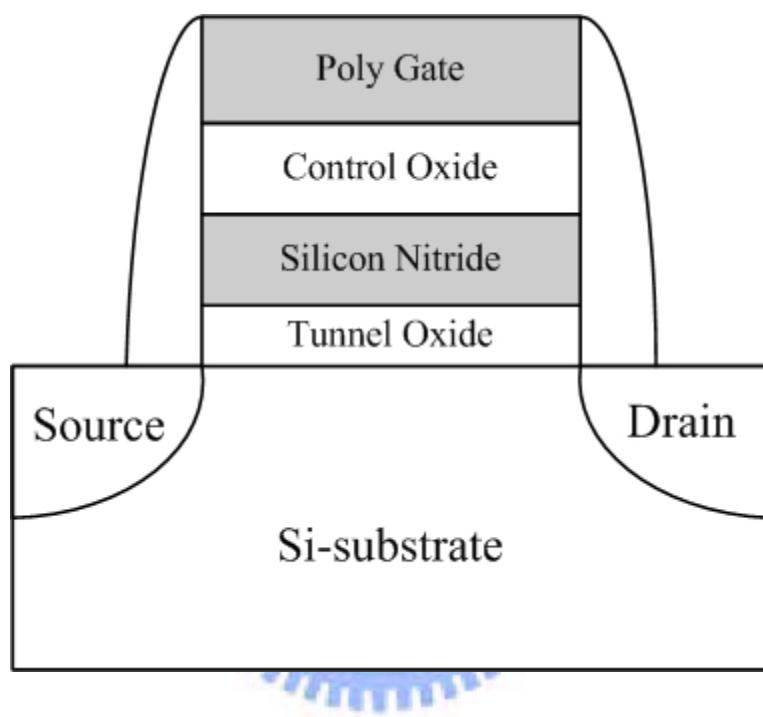


Figure 1-2 The structure of the SONOS nonvolatile memory device. The nitride layer is used as the charge storage element.

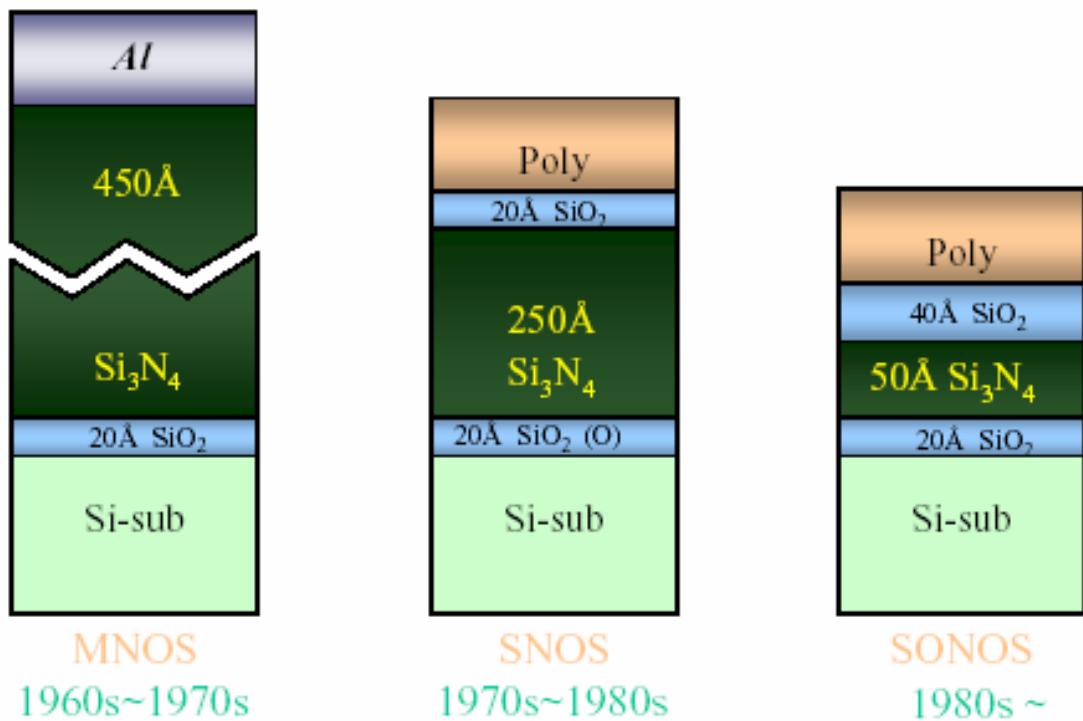


Figure 1-3 The development of gate stack of SONOS EEPROM memory devices. The optimization of nitride and oxide films has been main focus in recent years.

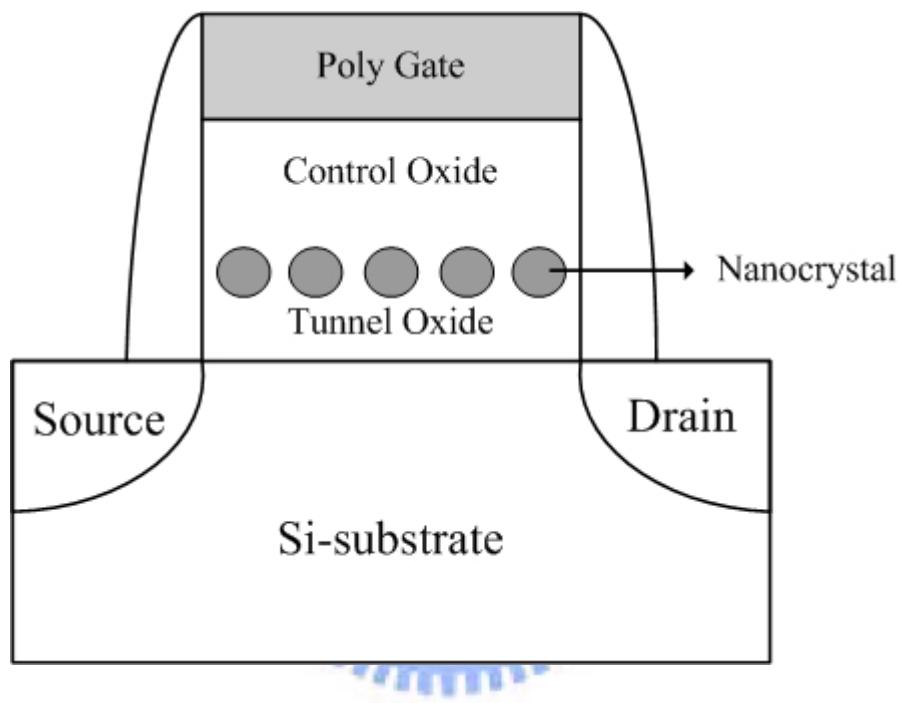


Figure 1-4 The structure of the nanocrystal (NC) nonvolatile memory device. The isolated nanocrystal with each other is used as the charge storage element.

Chapter 2

Nonvolatile Memory Basic Principles

2.1 Introduction

Most of operations on novel nonvolatile memories, such as SONOS and nanocrystal memories are base on the concept of Flash memory. If data was stored in selected cell of the memory, there are different procedures. The threshold voltage shift of a Flash transistor can be written as [2.1-2.2]:

$$\Delta V_T = -\frac{\bar{Q}}{C_{FC}}$$

where \bar{Q} is the charge weighted with respect to its position in the gate oxide, and the capacitances between the floating gate (FG) and control gate. The threshold voltage of the memory cell can be altered by changing the amount of charge present between the gate and the channel, corresponding to the two states of the memory cell, i.e., the binary values (“1” and “0”) of the stored bit. Figure 2-1 shows the threshold voltage shift between two states in a Flash memory. To a nonvolatile memory, it can be “written” into either state high state “1” or low state “0” by either “programming” or “erasing” methods, which are decided by the definition of memory cell itself. There are many solutions to achieve “programming” or “erasing”.

In this chapter, we will discuss program/erase mechanisms from the relation between bias and energy band bending. And different carrier injection mechanisms such as tunneling injection, channel hot electron injection and band to band tunneling. We will also discuss the reliability test briefly such as retention and endurance of NVM. Finally, some unique characteristic of nanocrystal memory will be discussed in the end of this chapter.

2.2 Basic Program/Erase Mechanisms

2.2.1 Energy band diagram during program and erase operation

The program/erase physical operation of a standard SONOS memory is illustrated in Figure 2-2. In the program operation, when a positive bias relative to the p-type substrate

applied on gate electrode, substrate induces an electron channel (inversion layer). Then the electron will tunnel through the tunnel oxide into the silicon nitride film and be trapped in deep level traps. Some electrons will not be trapped in the nitride film and will tunnel through the blocking oxide into gate electrode. The trapped electrons provide the electrostatic screening of the channel from the control gate, and result in a threshold voltage (V_T) shift. In the erase operation, when a negative bias relative to the p-type substrate applied on the gate electrode. The holes will tunnel through tunnel oxide into the nitride trapping layer and partially be trapped. Further, trapped electrons may be de-trapped into the nitride conduction band and then tunnel back to the channel. Thus, for SONOS memory device operation both carrier types are involved in the transport process.

Figure 2-3 illustrates schematically the write and erase operation of an n-channel nanocrystal memory. When the different bias applied on gate electrode, it causes different results. When the bias is positive relative to substrate, the electrons in the inversion layer inject in to the nanocrystal. That phenomenon is called “write operation”. On the contrary, negative bias applied to gate causes the electrons tunneling back to channel and the holes in the accumulation layer tunneling into the nanocrystal from the channel.

2.2.2 Carrier Injection Mechanisms

(a) Channel Hot Electron Injection (CHEI)

The physical mechanism of CHEI is relatively simple to understand qualitatively. An electron traveling from the source to the drain gains energy from the lateral electric field and loses energy to the lattice vibrations (acoustic and optical phonons). At low fields, this is a dynamic equilibrium condition, which holds until the field strength reaches approximately 10^5 V/cm [2-3]. For fields exceeding this value, electrons are no longer in equilibrium with the lattice, and their energy relative to the conduction band edge begins to increase. Electrons are “heated” by the high lateral electric field, and a small fraction of them have enough energy to surmount the barrier between oxide and silicon conduction band edges. Figure 2-4 shows schematic representation of CHEI MOSFET and the energy-distribution function with different fields.

In the other hand, the effective mass of hole is heavier than one of electron. It is too hard to obtain enough energy to surmount oxide barrier. Therefore, hot-hole injection rarely is employed in nonvolatile memory operation. For an electron to overcome this potential barrier, three conditions must hold [2.4].

- (1) Its kinetic energy has to be higher than the potential barrier.
- (2) It must be directed toward the barrier.
- (3) The field in the oxide should be collecting it.

Nevertheless, a description of the injection conditions can be accomplished with two different approaches. The CHEI current is often explained and simulated following the “lucky electron” model [2.5]. This model is based on the probability of an electron’s being lucky enough to travel ballistically in the field ϵ for a distance several times the mean free path without scattering, eventually acquiring enough energy to cross the potential barrier if a collision pushes it toward the Si/SiO₂ interface. Consequently, the probability of injection is the lumped probability of the following events [2.6], which are depicted in Figure 2-5.

- (1) The carrier has to be “lucky” enough to acquire enough energy from the lateral electric field to overcome the oxide barrier and to retain its energy after the collision that redirects the electron toward the interface ($P_{\Phi b}$).
- (2) The carrier follows a collision-free path from the redirection point to the interface (P_{ED}).
- (3) The carrier can surmount the repulsive oxide field at the injection point, due to the Schottky barrier lowering effect, without suffering an energy-robbing collision in the oxide (P_{OC}).

(b) Tunneling Injection

There are several tunneling mechanisms demonstrated in quantum mechanics. Basically, tunneling injection must have available states on the other side of the barrier for the carriers to tunnel into. The tunneling probability, depending on electron barrier height ($\phi(x)$), tunnel dielectric thickness (d), and effective mass (m_e) inside the tunnel dielectric, is express as [2.7]

$$T = \exp\left(-2 \int_0^d \frac{\sqrt{\phi(x) * m_e}}{\hbar} dx\right) \quad (2-1)$$

If we assume elastic tunneling, this is a reasonable assumption due to the thin oxide thickness involved. Namely, no energy loss during tunneling processes. Tunneling through the oxide can be attributed to different carrier-injection mechanisms. Which process applies depends on the oxide thickness and the applied gate field or voltage.

Direct tunneling (DT), Fowler-Nordheim tunneling (FN), modified Fowler-Nordheim tunneling (MFN) and trap assistant tunneling (TAT) are the main programming mechanisms employed in memory [2.8-2.10] as shown in Figure 2-6.

Direct Tunneling

For nanocrystal memories, the control-gate coupling ratio of nanocrystal memory devices is inherently small [2.11]. As a result, F-N tunneling cannot serve as an efficient program/erase mechanism when a relatively thick tunnel oxide is used, because the strong electric field cannot be confined in one oxide layer. The direct tunneling is employed in nanocrystal memories instead. And that makes the nanocrystal memory with lower operation voltage and faster program/erase speed. Generally speaking, a thinner tunnel oxide with thickness below 5 nm is used to separate the nanocrystal from channel. In the other hand, the direct tunneling is more sensitive to the barrier width than barrier height, two to four orders of magnitude reduction in leakage current can still be achieved if large work function metals, such as Au or Pt [2.12]. Figure 2-6(a) shows the both sides barrier relative to thickness of the oxide that make electron direct tunneling through the oxide.

Fowler-Nordheim Tunneling

The Fowler-Nordheim (FN) tunneling mechanism occurs when applying a strong electric field (in the range of 8–10 MV/cm) across a thin oxide. In these conditions, the energy band diagram of the oxide region is very sharp. Hence, there is a high probability of electrons' passing through the energy barrier itself. Using a free-electron gas model for the metal and the Wentzel–Kramers–Brillouin WKB approximation for the tunneling probability [2.13], one obtains the following expression for current density [2.14]:

$$J = \frac{q^3 F^2}{16\pi^2 h^2 \Phi_B} \exp\left[\frac{-4(2m_{ox}^*)^{1/2} \Phi_B^{3/2}}{3\hbar q F} \right] \quad (2-2)$$

Where Φ_B is the barrier height, m_{ox}^* is the effective mass of the electron in the forbidden gap of the dielectric, h is the Planck's constant, q is the electronic charge, and F is the electric field through the oxide. However, the exponential dependence of tunnel current on the oxide-electric field causes some critical problems of process control because, for example, a very small variation of oxide thickness among the cells in a memory array produces a great difference in programming or erasing currents, thus

spreading the threshold voltage distribution in both logical states. Figure 2-6(b) shows the both sides barrier relative to thickness of the oxide that make electron Fowler–Nordheim tunneling through the oxide.

Modified Fowler–Nordheim Tunneling

Modified Fowler–Nordheim tunneling (MFN) is similar to the traditional FN tunneling mechanism, the carriers enter the nitride at a distance further from the tunnel oxide-nitride interface. MFN mechanism is frequently observed in SONOS memories. The SONOS memory is designed for low-voltage operation (<10 V, depending on the Equivalent oxide thickness), a relatively weak electrical field couldn't inject charges by DT or FN mechanism. Figure 2-6(c) shows the both sides barrier relative to thickness of the oxide that make electron Modified Fowler–Nordheim (MFN) tunneling through the dielectric.

Trap Assistant Tunneling

The charge storage elements with many traps may cause another tunneling mechanism. For instance, the charges tunnel through a thin oxide and arrive to the traps of nitride layer at very low electrical field in SONOS systems. During trap assisted injection the traps are emptied with a smaller time constant then they are filled. The charge carriers are thus injected at the same distance into the nitride as for MFN injection. Because of the sufficient injection current, trap assisted tunneling may influence in retention [2.15]. Figure 2-6(d) illustrates the Trap Assistant Tunneling through the dielectric.

(c) Band to Band Tunneling (BTBT)

Band to band tunneling application to nonvolatile memory was first proposed in 1989. I. C. Chen and et al. demonstrated a high injection efficiency (~1%) method to programming EPROM devices [2.16]. Band to band tunneling (BTBT) process occurs in the deeply depleted doped surface region under the gate to drain or gate to source overlap region.

Band to Band Hot Electron Tunneling Injection

In n-type substrate, when band-bending is higher than the energy gap of the semiconductor, the tunneling electron from the valence band to the conduction band becomes significant. The electrons are accelerated by a lateral electric field toward the

channel region and some of the electrons with sufficient energy can surmount the potential barrier of SiO_2 like hot electron injection [2.16-2.18]. Figure 2-7 shows device operation during the band to band tunneling induced hot electron (BBHE) injection.

Band to Band Hot Hole Tunneling Injection

The injection is applied for p-type nonvolatile memory device. The mechanism is at the situation for both negative gate voltage and positive drain voltage. Electron-hole pairs are generated by BTBT in the drain region, as shown in Figure 2-8. The holes are accelerated by a lateral electric field toward the channel region and some of them obtain high energy. The hot holes with high energy will inject into charge trapping layer through the tunnel oxide and recombine with the stored electrons. This injection is used for a new erase operation for nonvolatile memory device [2.19].

2.3 Basic Reliability of Nonvolatile Memory

For a nonvolatile memory, the important to concern is distinguishing the state in cell. However, in many times operation and charges storage for a long term, the state is not obvious with charges loss. Retention and endurance experiments are performed to investigate Flash-cell reliability. In general, NVMs are required to achieve up to 10-100K program/erase cycles (endurance) with 10-year memory retention at temperatures as high as 85 °C.

2.3.1 Retention

Retention means that how long does the memory keep the information without losing it. In any nonvolatile memory technology, it is essential to retain data for over ten years. This means the loss of charge stored in the storage medium must be as minimal as possible. For example, in modern Flash cells, FG capacitance is approximately 1 fF. A loss of only 1 fC can cause a 1V threshold voltage shift. If we consider the constraints on data retention in ten years, this means that a loss of less than five electrons per day can be tolerated [2.1]. There are four possible causes of charge loss: 1) by tunneling or thermionic emission mechanisms; 2) defects in the tunnel oxide; and 3) de-trapping of charge from insulating layers surrounding the storage medium; 4) mobile ion contamination. Further, the retention capability of Flash memories has to be checked by using accelerated tests that usually adopt screening electric fields and hostile environments at high temperature.

2.3.2 Endurance

Endurance referred the number of erase/write operations that the memory will complete and continue to operate as specified in the data sheet. Generally speaking, Flash products are specified for 10^6 erase/program cycles. Nevertheless, the endurance requirement may be relaxed with the increase of memory density for the other using.

A typical result of an endurance test on a single cell is shown in Figure 2-9. As the experiment was performed applying constant pulses, the variations of program and erase threshold voltage levels are described as “program/erase threshold voltage window closure” and give a measure of the tunnel oxide aging [2.20-2.21]. In particular, the reduction of the programmed threshold with cycling is due to trap generation in the oxide and interface state generation at the drain side of the channel. The evolution of the erase threshold voltage reflects the dynamics of net fixed charge in the tunnel oxide as a function of the injected charge. The initial lowering of the erase is due to a pile-up of positive charge which enhances tunneling efficiency, while the long-term increase of the erase is due to a generation of negative traps.

Moreover, a high field stress on thin oxide is known to increase the current density at low electric field. The excess current component, which causes a significant deviation from the current–voltage curves from the theoretical F-N characteristics at low field, is known as stress-induced leakage current (SILC). SILC is clearly attributed by stress-induced oxide defects, which leads to a trap assisted tunneling. The main parameters controlling SILC are the stress field, the amount of charge injected during the stress, and the oxide thickness. For fixed stress conditions, the leakage current increases strongly with decreasing oxide thickness [2.22-2.24].

2.4 Basic Physical Characteristics of Nanocrystal Memory

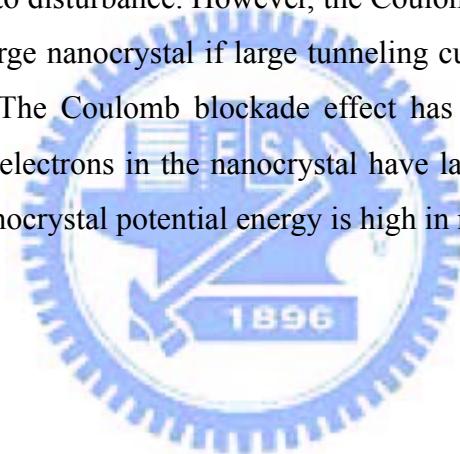
2.4.1 Quantum Confinement Effect

The quantum dot, is quasi-zero-dimensional nanoscaled material, and is composed by small amount atoms. The quantum confinement energy dependence on nanocrystal size has been studied both experimentally and theoretically with the tight-binding model [2.25]. The quantum confinement effect becomes significant when the nanocrystal size shrinks to the nanometer range, which causes the conduction band in the nanocrystal to shift to higher energy compared with bulk material [2.26]. For instance, a 3nm Ge nanocrystal can have a conduction band shift up 0.5eV as compared with bulk Ge, which

is significant enough to affect the electrical performance of the nanocrystal memory cell.

2.4.2 Coulomb Blockade Effect

With a electron is stored, the nanocrystal potential energy is raised by the electrostatic charging energy $e^2/2C$, where C is the nanocrystal capacitance, which depends mainly on the nanocrystal size, though it also depends on tunnel oxide thickness and control oxide thickness. The capacitance is self-consistently calculated using an electrodynamics method [2.27]. Charging electrons will raise the nanocrystal potential energy and reduce the electric field across the tunnel oxide, resulting in reduction of the tunneling current density during the write process. It is more dominant at low programming voltages ($< 3V$). In a flash memory array, device cells often encounter disturbances with low gate voltage soft-programming. The Coulomb blockade effect can effectively inhibit the electron tunneling at low gate voltage and improve the flash memory array immunity to disturbance. However, the Coulomb blockade effect should be reduced by employing large nanocrystal if large tunneling current and fast programming speed were considered. The Coulomb blockade effect has a detrimental effect on the retention time, since the electrons in the nanocrystal have large tendency to tunnel back into the channel if the nanocrystal potential energy is high in retention mode.



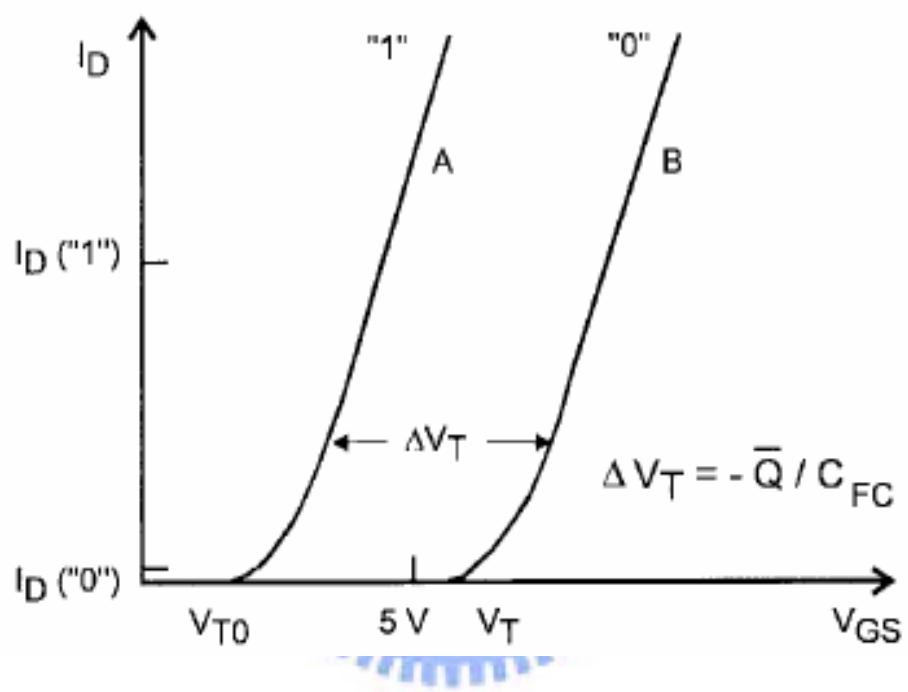


Figure 2-1 I_D - V_{GS} curves of the floating-gate NVM device, with before (curve A) and after (curve B) negative charge \bar{Q} is stored in the floating gate.

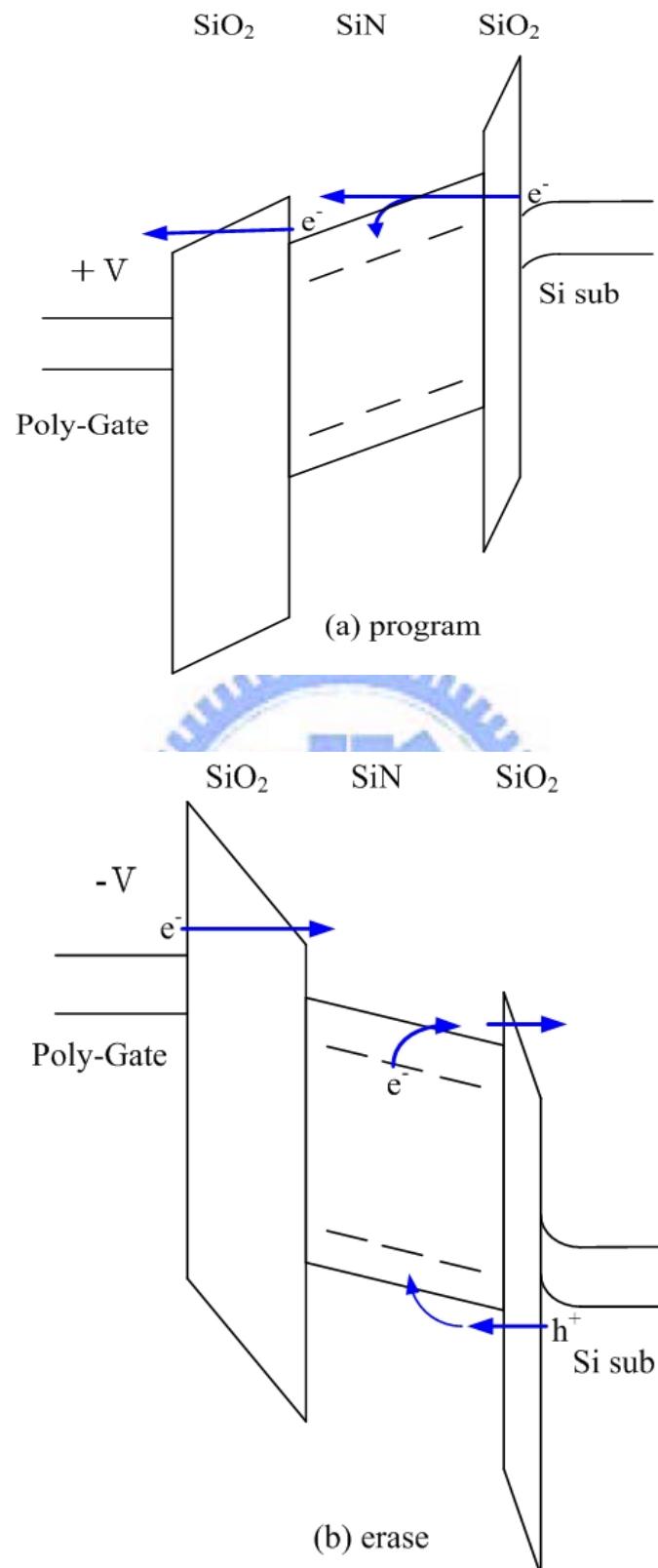


Figure 2-2 Energy band diagrams of the SONOS memory device under (a) program (b) erase operation. (e^- : electrons, h^+ : holes.)

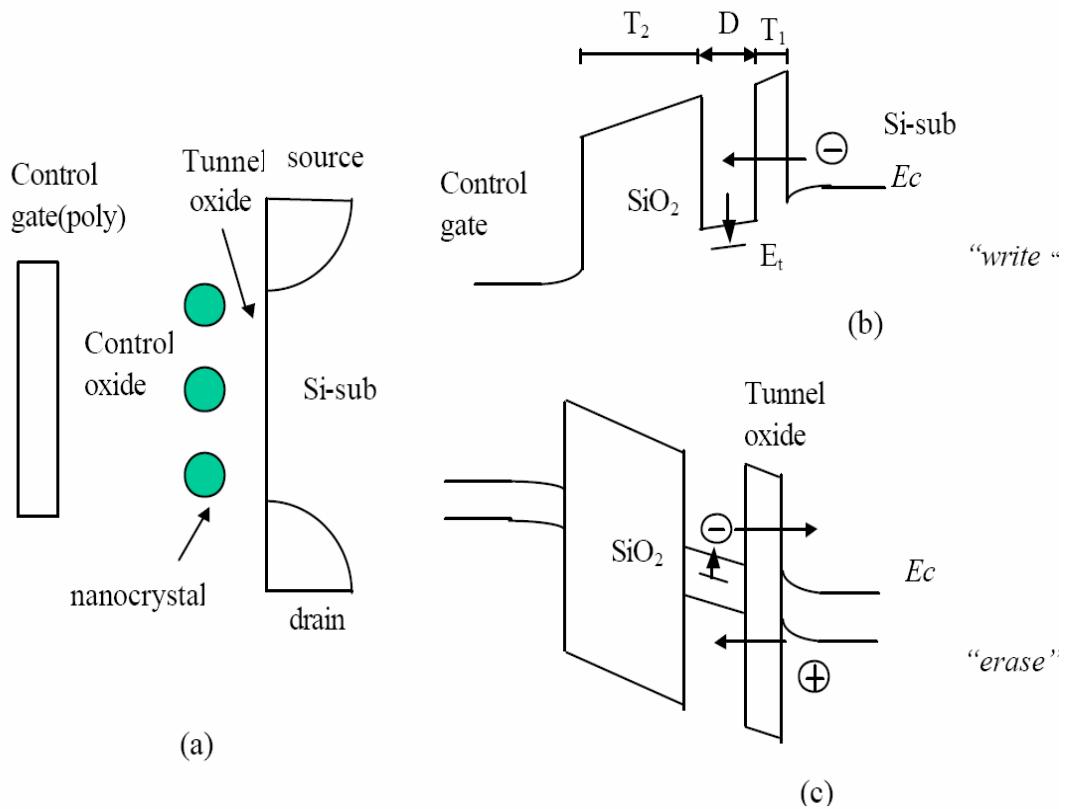


Figure 2-3 (a) The cross-section of nanocrystal memory device structure; (b) illustration of write process: inversion-layer electrons tunnel through tunnel oxide and inject into the nanocrystal; (c) illustration of erase process: accumulation layer holes tunnel through tunnel oxide and inject into the nanocrystal, electrons in nanocrystal also can tunnel back to the channel.

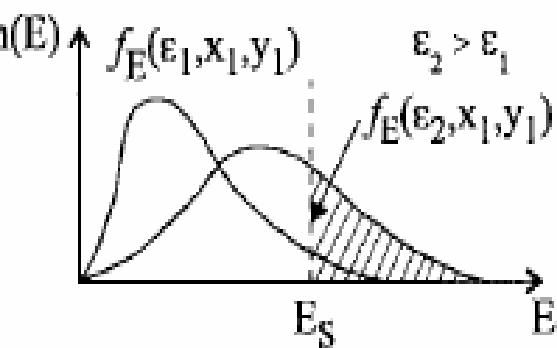
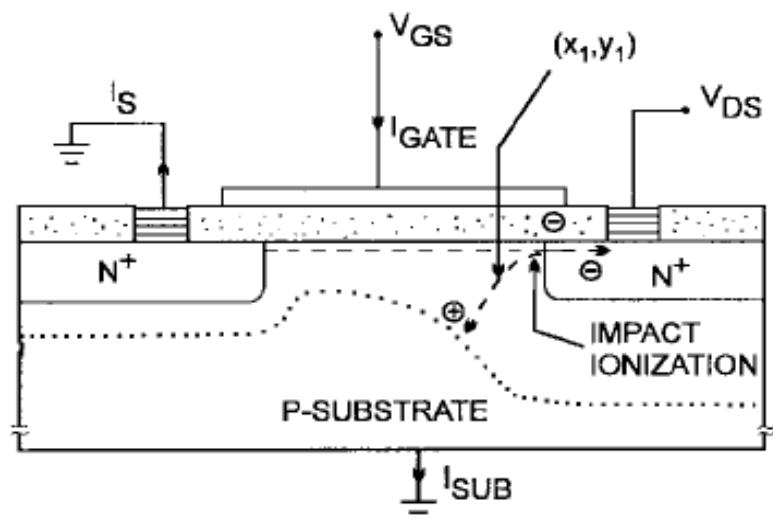


Figure 2-4 Schematics of channel hot electron injection (CHEI). The energy distribution function at point (X_1, Y_1) is also shown.

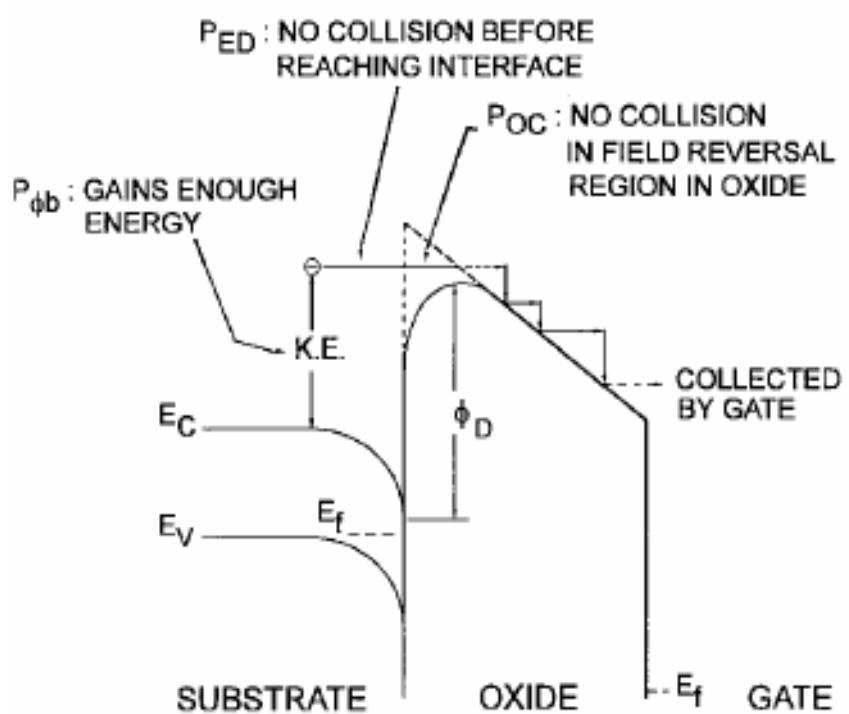
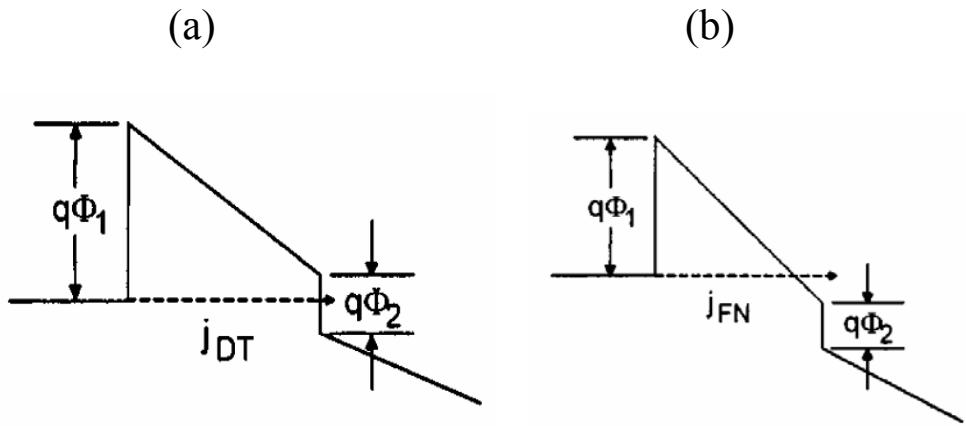
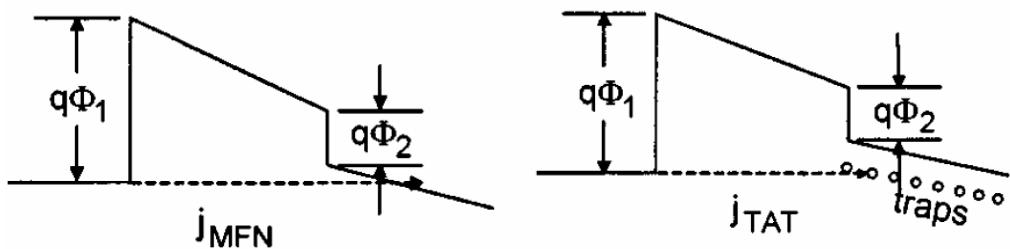


Figure 2-5 A schematic energy band diagram describing the different processes involved in electron injection.



DT occur when $\frac{\phi_1}{X_{OT}} > |E_{OT}| > \frac{\phi_1 - \phi_2}{X_{OT}}$ FN occur when $|E_{OT}| > \frac{\phi_1}{X_{OT}}$



MFN occur when

$$\frac{\phi_1 - \phi_2}{X_{OT}} > |E_{OT}| > \frac{\phi_1 - \phi_2}{X_{OT} + \left(\frac{\epsilon_{ox}}{\epsilon_N}\right)X_N}$$

TAT occur when

$$\frac{\phi_3}{X_{OT}} > |E_{OT}| > \frac{\phi_3}{X_{OT} + \left(\frac{\epsilon_{ox}}{\epsilon_N}\right)X_N}$$

$$\phi_3 = \phi_1 - \phi_2 - \phi_t$$

Figure 2-6 Fourth approaches to programming methods (a) Direct tunneling (DT) (b) Fowler-Nordheim (FN) tunneling (c) Modified Fowler-Nordheim (MFN) tunneling (d) Trap assistant tunneling (TAT).

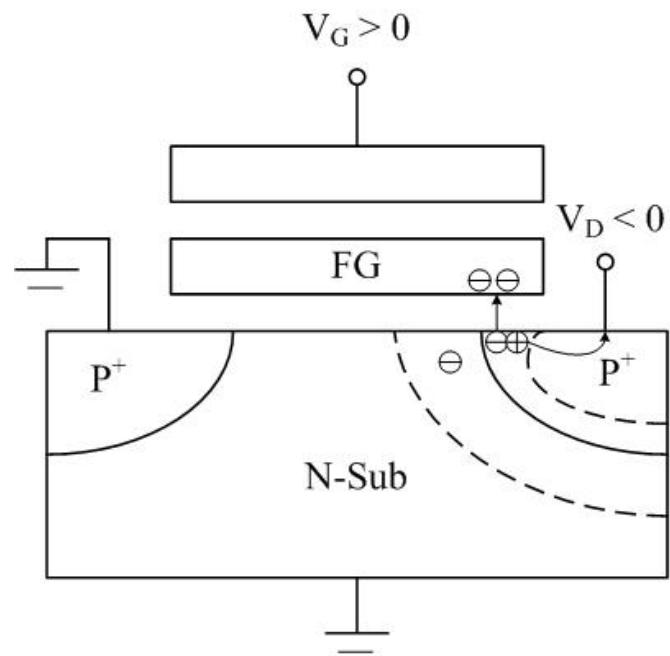


Figure 2-7 The procedure of band to band hot electron injection.

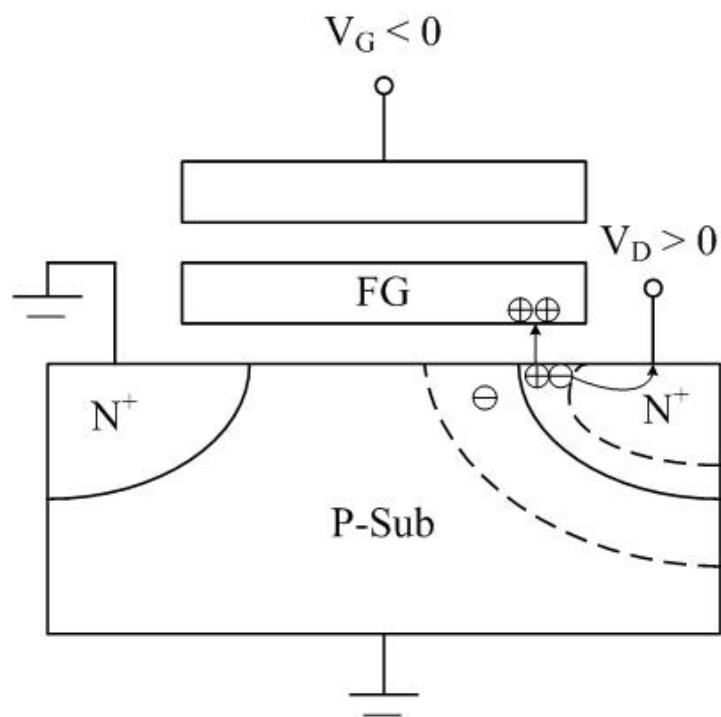


Figure 2-8 The procedure of band to band hot hole injection.

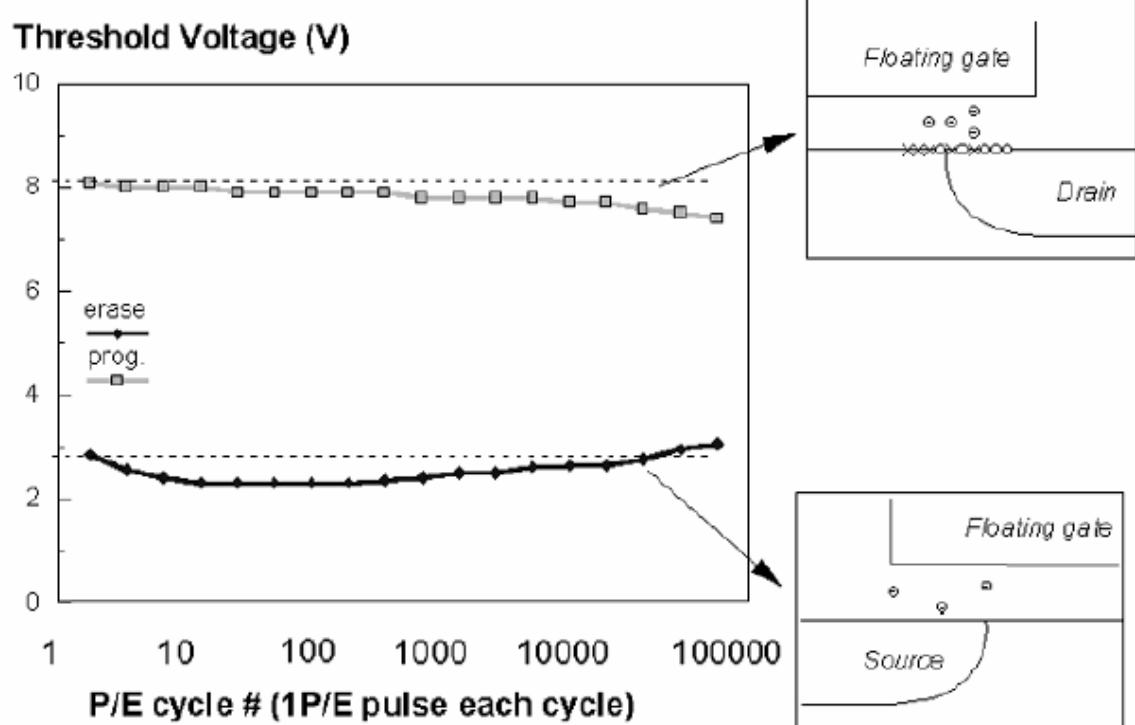


Figure 2-9 A typical result of an endurance test on a single cell. Threshold voltage window closure as a function of program / erase cycles.

Chapter 3

Formation of Germanium Nanocrystals Embedded in Silicon Oxide Layer

3.1 Introduction

The nonvolatile memory (NVM) for portable electronic productions play an important role in semiconductor industrial because of its superiority in low-power consumption, low-cost, high-memory capacity and enough data retention[3.1][3.2]. The conventional NVM, however, can't efficaciously prevent data loss in terms of reliability trials for future scaling down process, since its charge trapping layer is fabricated by floating gate (FG) structure and its tunnel oxide is ultra thin film about 2-5 nm[3.3][3.4]. Due to the discrete charge storage nodes acting as charge trapping layer to reform drawbacks of conventional FG memory, the NVMs using various semiconductor nanocrystals have been widely investigated in the past few years , such as silicon (Si) , germanium (Ge) and Zine-Oxide (ZnO) nanocrystals[3.2][3.5]. Moreover, in order to improve operation speed one can replace silicon nanocrystals (NC-Si) by germanium nanocrystals (NC-Ge) thanks to its higher dielectric constant (~16.0, i.e., stronger coupling with the conduction channel). In the other way, Ge nanocrystals device will improve data retention time due to its smaller energy band gap. Indeed King et al. [3.6] have reported recently superior properties for NC-Ge base on memory over than NC-Si in terms of writing/erasing time.

According to the current research, the self-assembled and direct growth of Ge nanocrystals embedded in SiO_2 layer has successfully been implemented such as Ge implantation into SiO_2 [3.7-3.8], oxidation reduction of Ge/Si islands [3.9], UV-assisted oxidation of $\text{Si}_{1-x}\text{Ge}_x$ alloy [3.10], and rapid thermal oxidation (RTO) of NC-Ge [3.11-3.12] or Ge + SiO_2 [3.13]. Among various formation methods, the self-assembled was reported by many previous studies because it could control better density and size of nanocrystal than direct growth. Nevertheless, the self-assembled method must need a high temperature (~900-1100°C) with long duration (~30-60 min) oxidation process to

anneal the charge trapping layer that is deposited by various ratio of SiGe layer, and the over-oxidation phenomenon of Ge is often obtained after foregoing oxidation process. Hence, an additional step must be added to the formation flow of Ge nanocrystal by using a high pressure H₂ treatment [3.14-3.15] or steam process [3.16].

In order to reduce process flow and thermal budget, we choose the sputter system and rapid thermal anneal (RTA) for our experiments.

3.2 Growth SiGe and oxidation

There were a lot of experiments forming Ge nanocrystal by oxidizing the SiGe film. The SiGe film might be deposited by different process such as low pressure chemical vapor deposition (LPCVD), sputter system, plasma enhanced chemical vapor deposition (PECVD). At the same, we tried to deposit SiGe thin film by co-sputter and thermal treatment.

3.2.1 Experimental Sample Preparation

Figure 3-1 shows schematics of the experimental process flow. This nonvolatile memory-cell structure in this study was fabricated on a 4 inches p-type silicon (100) wafer, which had been removed native oxide and particles by RCA process. After a standard RCA clean, a 3-nm-thick tunnel oxide was thermally grown by a dry oxidation process at 950°C in an atmospheric pressure chemical vapor deposition (APCVD) furnace. Subsequently, a 7-nm-thick SiGe film was deposited on tunnel oxide by co-sputtering Si and Ge targets in Argon (Ar) ambience at room temperature, and the Ar flow rate was set to 24 sccm (Standard Cubic Centimeter per Minute). And then we deposited a 10-nm-thick pure amorphous Si by sputtering Si target in pure Ar ambience. And then we oxidized the sample by rapid thermal anneal (RTA) at 900°C 60sec in Oxygen ambience. Expected Germanium nanocrystal could be found to precipitate and embed in silicon oxide. During the rapid thermal oxidation (RTO) process, the Si layer capped on the SiGe film was formed blocking oxide at the same time. Al gate electrodes on back and front side of the sample were finally deposited and patterned to form a metal/oxide/insulator/oxide/silicon (MOIOS) structure.

Electrical characteristics of the capacitance-voltage (C-V) hysteresis were measured by Keithley 4200 and HP4284 Precision LCR Meter with high frequency 1 MHz. In addition, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) were adopted for the micro-structure analysis and chemical material analysis.

3.2.2 Results and Discussion

Figure 3-2 shows the TEM of the sample after RTO process. We can find out the charge trapping layer became a continuous film. The XPS analysis by using an Al $K\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the charge trapping layer, as shown in figure 3-3. From the Ge 2p core-level spectrum, we can see that the GeO_2 peak is at about 1220 eV by fitting results. Therefore, we think the entire trapping layer was over-oxidized and the Ge layer all became GeO_2 . The capacitance-voltage (C-V) hysteresis is shown in figure 3-4. It is clearly observed that 0.5V memory window was obtained under ± 5 V gate voltage operation. And the hysteresis loops follow the counterclockwise due to injection of electrons from the deep inversion layer and discharge of electrons from the deep accumulation layer of Silicon substrate. Hence, we can be enough to define “1” and “0” states for nonvolatile memory application. Figure 3-5 shows the band diagram of our sample after RTO 900°C 60sec. GeO_2 energy band gap is about 4 eV [3.17]. Due to GeO_2 providing some charge traps and the interface trap with tunnel oxide, this sample still has memory effect.

According to the previous experiment result, we can find out some results: (1) the co-sputter method is hard to control the Si/Ge ratio; (2) conventional oxidation of SiGe layer is hard to control the oxidation time; (3) as our sample, the Ge was all oxidized and became GeO_2 likes the below formula.



There are some drawbacks from the above results, in ordering to solve the over oxidation problem. We propose a SiGeO film on tunnel oxide to avoid over-oxidation phenomenon.

3.3 Formation of Ge nanocrystal using SiGeO layer

3.3.1 Experimental Sample Preparation

This nonvolatile memory-cell structure in this study was fabricated on a 4 inches p-type silicon (100) wafer, which had been removed native oxide and particles by RCA process. After a standard RCA clean, a 5-nm-thick tunnel oxide was thermally grown by a dry oxidation process at 950°C in an atmospheric pressure chemical vapor deposition (APCVD) furnace. Subsequently, a 8-nm-thick oxygen incorporated $\text{Si}_x\text{Ge}_{1-x}$ (SiGeO) layer was deposited on tunnel oxide by reactive sputtering of $\text{Si}_x\text{Ge}_{1-x}$ commixed target in the Ar/O_2 (24sccm/2sccm) ambiance at room temperature. This step can obtain an oxygen

incorporated $\text{Si}_x\text{Ge}_{1-x}$ layer as a charge trapping layer in our memory.

We choose two different ratio of Si/Ge. One is $\text{Si}_{0.8}\text{Ge}_{0.2}$ and the other is $\text{Si}_{0.5}\text{Ge}_{0.5}$. $\text{Si}_{0.8}\text{Ge}_{0.2}$ is a common ratio for LPCVD to form Ge nanocrystals (NCs) [3.18]. However its density of NCs is about 10^{11}cm^{-2} . In order to achieve higher density of NCs, we choose a higher Ge concentration target ($\text{Si}_{0.5}\text{Ge}_{0.5}$) and then we noted the first process with using $\text{Si}_{0.8}\text{Ge}_{0.2}$ target “Sample I”. The other one with $\text{Si}_{0.5}\text{Ge}_{0.5}$ was noted “Sample II”.

After that, we annealed the above two sample by rapid thermal anneal (RTA) at 900°C 30sec in Nitrogen ambience. The RTA process was performed to cause the self-assembled of Ge nanocrystal in the charge trapping layer. After RTA process, a 30-nm-thick blocking oxide was deposited by PECVD at 300°C . Al gate electrodes on back and front side of the sample were finally deposited and patterned to form a metal/oxide/insulator/oxide/silicon (MOIOS) structure. Figure 3-6 (a) and (b) show schematics of the experimental process flow.

In addition, after the two different ratio of SiGeO film was deposited, we deposited a 20-nm-thick PECVD oxide on it. This step was called PACO (pre-annealing-capping-oxide). And then we annealed our sample by RTA at 900°C 30sec or 60sec in N_2 ambience. The RTA process was performed to cause the self-assembled of Ge nanocrystal in the charge trapping layer. After RTA process, a 20-nm-thick blocking oxide was deposited by PECVD at 300°C . Al gate electrodes on back and front side of the sample were finally deposited and patterned to form a metal/oxide/insulator/oxide/silicon (MOIOS) structure. Figure 3-7 (a) (b) shows schematics of the experimental process flow.

Electrical characteristics, including the capacitance-voltage (C-V) hysteresis, current density-voltage (J-V), retention, and endurance characteristics, were also performed. The J-V and C-V characteristics were measured by Keithley 4200 and HP4284 Precision LCR Meter with high frequency 1 MHz. In addition, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) were adopted for the micro-structure analysis and chemical material analysis.

3.3.2 Results and Discussion

The XPS analysis by using an $\text{Al K}\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the sample I ($\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$), as shown in figure 3-8. Figure 3-8 (a), (b), (c) show Si 2p, Ge 3d, O 1s core-level spectra. We can roughly define the trapping

layer atomic composition of sample I by a common method. For example, we calculate the Ge concentration of the SiGeO film by below formula:

$$[Ge] \simeq \frac{I_{Ge3d}/S_{Ge3d}}{I_{Si2p}/S_{Si2p} + I_{Ge3d}/S_{Ge3d} + I_{O1s}/S_{O1s}} \quad (3-2)$$

The “I” means the peak intensity, and “S” the material sensitivity of the ESCA. The atomic concentration with silicon, germanium and oxygen of the charge trapping layer are 34.3%, 3.5%, and 62.2%, as table 3-1 shown. We can observe that oxygen was successfully incorporated in charge trapping layer during sputter process and the Ge concentration is deficient.

As the same, figure 3-9 (a), (b), (c) exhibit the Si 2p, Ge 3d, O 1s core-level spectra of the sample II ($Si_{0.5}Ge_{0.5}O$). And we use the same method to define the atomic concentration roughly. The atomic concentration with silicon, germanium and oxygen of the charge trapping layer are 32%, 16.8%, and 51.2%, as table 3-2 shown. We can also observe that oxygen was successfully incorporated during sputter process but the Ge concentration is more than sample I.

Figure 3-10 shows the transmission electron microscope (TEM) diagram of the control $Si_{0.5}Ge_{0.5}O$ sample (sample II). We can figure out a continuous and uniform SiGeO film was deposited on the tunnel oxide.

Figure 3-11 (a) and (b) show the capacitance-voltage hysteresis of control sample I and control sample II (without any thermal treatment). It is obviously that both of the control samples show no memory effect. Figure 3-12 (a) and (b) show the C-V hysteresis of both sample I and II after RTA 900°C 30sec in nitrogen ambience. The electrical C-V measurements were performed by bidirectional voltage sweeping. The sweeping condition were split as follows, (i) from 5V to -5V, and reversely, (ii) from 10V to -10V, and reversely. However, our samples still show no memory effect after thermal treatment as figure 3-11 (a) and (b) shown. Figure 3-13 show the TEM diagram of the sample II after RTA 900°C 30sec in nitrogen ambience. From figure 3-13, we could find out some Ge atom was self-assembled. Compare figure 3-13 with figure 3-10, the charge trapping layer was no longer a continuous film after RTA process. And the Ge concentration seems to become less after RTA process. Therefore, we made some secondary ion mass spectrometer (SIMS) analysis for our sample. Figure 3-14 (a) and (b) exhibit the SIMS analysis for sample II ($Si_{0.5}Ge_{0.5}O$) before and after RTA process. What should we

concern is the Ge concentration of these two sample. Ge secondary ions counts is over 10^5 before RTA, but became just between 10^3 and 10^4 after RTA. In order to compare their difference clearly, we put them on the same picture. Figure 3-14 (c) shows both Ge concentrations before and after RTA process. Obviously, Ge secondary ions counts decrease about two orders after thermal treatment. We think that is because Ge got bonded with oxygen during the RTA process, and GeO is a kind of volatile compound. Hence, the Ge was out-gassing and left the surface [3.19]. As the Ge becomes less, there is not enough Ge to be self-assembled. Therefore, we deposited a 20-nm-thick oxide by PECVD to avoid GeO out-gassing before thermal treatment. We call this step pre-annealing capping oxide (PACO).

As the previous process flow we have mentioned, figure 3-15 show C-V hysteresis of the sample I ($\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$) after RTA 900°C 30sec in nitrogen ambience with PACO. It shows memory effect, when we capped PECVD oxide before RTA process. Under $\pm 10\text{V}$ operation, the Flat-band voltage shift (memory window, ΔV_{FB}) is about 0.65V . And the hysteresis loops follow the counterclockwise due to injection of electrons from the deep inversion layer and discharge of electrons from the deep accumulation layer of Silicon substrate. Hence, we can be enough to define “1” and “0” states using this nonvolatile memory. Figure 3-16 (a) and (b) show the TEM diagram of the sample I ($\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$) after RTA with PACO. From the figure 3-16 (b), Ge was segregated and nucleated obviously. And the Ge dot size is about $4\text{--}6\text{ nm}$. Moreover, the lattice image is shown in the figure 3-16 (a). We can easily observe that Ge was self-assembled from the TEM picture, but why the memory effect is not so obvious. Figure 3-17 exhibits the SIMS analysis of the sample I after RTA with PACO. From the SIMS analysis, we can presume that the memory effect is not obvious due to there is not sufficient Ge.

With the previous results, increasing the Ge concentration seems indeed to enlarge the memory effect. Figure 3-18 shows C-V hysteresis of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA 900°C 30sec in nitrogen ambience with PACO. The electrical C-V measurements were performed by bidirectional voltage sweeping. The sweeping condition were split as follows, (i) from -5V to 5V , and reversely, (ii) from -10V to 10V , and reversely. Under $\pm 10\text{V}$ sweeping operation, the Flat-band voltage shift (memory window, ΔV_{FB}) is about 2.8V . When the device is programmed, the electrons directly tunnel from the Si substrate through tunnel oxide, and are trapped in the forbidden gap of Ge nanocrystal embedded in the SiO_x layer. For the erasing step, the holes may tunnel from the valance band of Si substrate and recombine with the electrons trapped in the Ge nanocrystals embedded SiO_x .

layer. The stacked structure with Ge nanocrystals in the dielectric layer was used for the application of memory. The charge trap canters are believe to be resulted from the (i) interface states between the silicon substrate, (ii) traps inside the dielectric layer, (iii) nanocrystal confined state, (iv) interface states between nanocrystals and the surrounding dielectric[3.20].

Figure 3-19 (a) and (b) show the TEM diagram of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA 900°C 30sec with PACO. From the figure 3-19 (b), Ge was segregated and nucleated obviously. The average diameter of the nanocrystals is approximately 5-6 nm and the area density of the nanocrystals is estimated to be about $1.73 \times 10^{12} \text{ cm}^{-2}$ by TEM analysis. Moreover, the lattice image is shown in the figure 3-19 (a). In the figure 3-19 (a), we can find out a common phenomenon about Ge diffused toward the SiO_x or SiO_2 in our experiment. Figure 3-20 shows SIMS analysis with sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) before and after RTA process. It clearly exhibits the Ge will diffuse in the silicon oxide. Because of our thermal treatment using RTA which lower thermal budget, that made Ge's diffusion length be limited. And all the Ge atoms were confined in the region we want. Figure 3-21 (a) (b) (c) show the relationship with different ratio of Si/Ge and their electrical characteristics. We can figure out that sample I's memory window under $\pm 10\text{V}$ operation is smaller the sample II's one with the same thermal treatment condition. Hence, we make a comment about that if we want to form Ge nanocrystal for charge storage elements; we need sufficient Ge of course.

In order to improve the performance of Germanium nanocrystal memory, we extended the annealing duration of RTA process from 900°C 30sec to 900°C 60sec. Figure 3-22 shows C-V hysteresis of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA 900°C 60sec in nitrogen ambiance with PACO. The electrical C-V measurements were performed by bidirectional voltage sweeping. The sweeping condition were split as follows, (i) from -5V to 5V , and reversely, (ii) from -10V to 10V , and reversely. Under $\pm 10\text{V}$ sweeping operation, the Flat-band voltage shift (memory window, ΔV_{FB}) is about 3.1V . Figure 3-23 (a) and (b) show the TEM diagram of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA 900°C 60sec with PACO. From the figure 3-23 (b), Ge was segregated and nucleated obviously. The average diameter of the nanocrystals is approximately 4-8 nm and the area density of the nanocrystals is estimated to be about $1.26 \times 10^{12} \text{ cm}^{-2}$ by TEM analysis. Moreover, the lattice image is shown in the figure 3-23 (a). Compare figure 3-23 (b) with figure 3-19 (b), we can discover that the nucleation and isolation of Ge nanocrystals became better after

longer thermal treatment. That is the reason for 900°C 60sec sample has larger memory window than the other.

According the above electrical characteristics, we make a table to compare the performance with each other. Table 3-3 shows the memory window under ± 10 V operation with different condition. We can find out some results from this table: (i) Pre-annealing-capping oxide (PACO) which can avoid GeO out-diffusion is a critical step in our process. (ii) Germanium nanocrystals density and memory window are related to Ge concentration. (iii) Longer thermal treatment make Germanium be better isolated and nucleated. (iv) High pressure hydrogen annealing could be replaced by RTA SiGeO film to simplify the process flow and reduce fabrication cost.

3.4 Mechanism of Germanium Nanocrystal Formation by thermal treatment

In this section, we will discuss the mechanism of Ge nanocrystals formation by thermal treatment.

3.4.1 Reaction free energy

In pure O₂, oxidation of silicon and germanium, forming SiO₂ and GeO₂, occurs following the reaction:

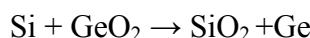


With a free energy change of $\Delta G_1 = -732.94 \text{ kJmol}^{-1}$, whereas for

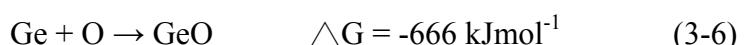


With a free energy change of $\Delta G_2 = -377.54 \text{ kJmol}^{-1}$.

The lower value of ΔG_1 ($< \Delta G_2$) clearly predicts that the SiO₂ reaction is thermodynamically more preferable than GeO₂. Thermodynamically, GeO₂ is not stable in the presence of silicon. Thus, during the simultaneous oxidation process reduction reaction takes place at the reaction interface, forming more SiO₂ while liberating germanium from GeO₂, as long as silicon is available [3.21], i.e.,



On the other hand, we use Gibbs free energy to explain our result.

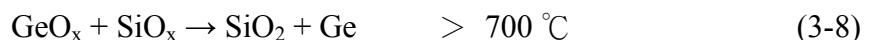
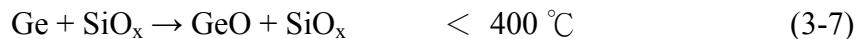


From the above equations [3.22], because of the smaller Gibbs free energy of Si–O compared with Ge–O, the oxygen atoms can interact with Si atom easier than with Ge

atom in the SiGeO ternary film during the RTA process.

3.4.2 Results and discussion

Base on the previous study, we know that Ge may get bonded with oxygen from SiO₂ when the temperature below 400°C. GeO is a volatile material, therefore when the temperature over 400°C, it will become gas state. And the temperature getting higher, over 700°C, Ge will be self-assemble in the SiO₂. The above phenomena are stated in below equation [3.23] :



During the thermal treatment, Si atoms will move and bond with oxygen result in Ge segregate and self nucleate forming nanocrystals. As the equation 3-8, we also observe the result in our experiment. Figure 3-24 show the X-ray photoelectron spectroscopy (XPS) analysis. In the Ge 3d core-level spectrum, the peak is at about 31eV which means the Ge-O bond as deposited. And after RTA, the peak position move toward 29eV which means Ge-Ge bond.

3.5 Reliability of the Germanium Nanocrystal Embedded Silicon Oxide Nonvolatile Memory

The reliability characteristics retention time and endurance were also discussed in this study. And as the previous discussion, we know that only sample II (Si_{0.5}Ge_{0.5}O) with PACO process have better electrical characteristics. Thus we will only discuss the better performance conditions.

Retention characteristics of the MOIOS structure with Ge nanocrystals embedded in the SiO_x are illustrated in figure 3-25 (a) and (b). The retention measurements are performed at room temperature by operating a ±15V gate voltage stress for 10 sec. The flat-band voltage shift is obtained by comparing the C-V curves from a charged state to the quasi-neutral state. When the carriers are stored in the nanocrystals, the stored charges will raise the nanocrystal potential energy and increase the probability of escaping from the nanocrystal to silicon substrate or gate. Figure 3-25 (a) shows retention time of the sample II with PACO and RTA 900°C 30s. The memory window decays during the stored charges leaked out from the nanocrystals to substrate or gate. Finally, a 0.36 V memory window (charge remained ratio is about 9.6%) from the elongation line of the decay trend can obtain even after 10 years. Figure 3-25 (b) shows retention time of the sample II with

PACO and RTA 900°C 60s. The memory window decays during the stored charges leaked out from the nanocrystals to substrate or gate. Moreover, a 1.15 V memory window (charge remained ratio is about 25%) from the elongation line of the decay trend can obtain even after 10 years. It retains a large window of 1.15V which is enough to define “1” or “0” of memory state.

It is easily observed the sample with longer thermal treatment (RTA) condition shows better retention time. As we know there are three leakage path for the charge leaking out of the nanocrystal. The first one is leaking out through the blocking oxide to gate electrode. The second one is leaking out through the tunnel oxide to the substrate. Finally the third one is called lateral leakage due to connected Ge which does not isolate well or the defects in the SiO_x dielectric enhanced leakage.

Figure 3-26 (a) and (b) exhibits band diagram during measurement and the current density – voltage characteristics. From the figure 3-26 (a), we can find out the blocking oxide quality dominate the magnitude of the current density. And the figure 3-26 (b) shows the current density of the 900°C 30sec and 900°C 60sec were similar. Hence we can consider that the quality of the both sample are almost the same. Therefore, the leakage path one (from top blocking oxide) is not the reason to cause the retention data worse of shorter annealing time sample.

Endurance characteristics of the MOIOS structure with Ge nanocrystals embedded in the SiO_x are illustrated in figure 3-27 (a) and (b). Pulses ($V_G = \pm 5V$, 1ms) were applied to evaluate endurance characteristics for the Program/Erase operation. Both of the (a) 900°C for 30sec and (b) 900°C for 60sec still show a better endurance performance after 10^6 program/erase cycles. Form the results of endurance measurements, we can find out the tunnel oxide and the dielectric below nanocrystal have good quality of both sample. According to that, the leakage path two (from bottom tunnel oxide) is not the main factor to affect retention time. Thus the lateral leakage dominates the retention characteristics. And the lateral path is related to the Ge nanocrystal isolation and the defects in the SiO_x dielectric.

The comparisons of memory window under $\pm 10V$ sweeping operation and memory window after 10 years of Ge nanocrystal embedded in SiO_x MOIOS structure between different thermal treatment (RTA) times were listed in Table 3-4. The 900°C 60s sample shows larger memory window the 30s one. That is because the longer thermal treatment induces the better isolation and nucleation of Ge. And longer thermal treatments not only make Ge isolated and nucleated better, but also reduce the defects in

the SiO_x dielectric. And as we know, the defects in the SiO_x can afford additional charge traps [3.24]. However, after reducing the defects by longer RTA process, we still get larger memory window. That is because the charging carrier ability in the Ge is better than defect traps in the dielectric.

3.6 Summary I

From the above experiments result, we successfully incorporated oxygen into SiGe layer forming a new dielectric SiGeO film by sputtering a commixed target ($\text{Si}_x\text{Ge}_{1-x}$) in an Ar/O₂ environment at room temperature. After some failed experiments, we find out the “pre-annealing capping oxide (PACO)” is a critical step in our process flow. The self-assembled phenomenon of Germanium nanocrystal can be explained by the chemical free energy. The Ge nanocrystals embedded in SiO_x memory was fabricated easily. And the high density ($\sim 10^{12}$) of Ge nanocrystals can be achieved in this study. We observed that longer thermal treatment (RTA) can improve the isolation and nucleation of Ge nanocrystals. The memory window of RTA 900°C 60s condition is 3.2V under $\pm 10\text{V}$ sweeping operation. And the memory window is large enough to define high and low states for nonvolatile memory application. The retention and endurance characteristics are good enough to be maintained up to 10 years and 10^6 program/erase cycles. In addition, this novel and simple fabrication technique of germanium nanocrystals could be compatible with current manufacture process of the integrated circuit manufacture.

Surface Atomic Concentration Ratio from XPS Analysis		
Si	Ge	O
34.3%	3.5%	62.2%

Table 3-1 Surface atomic concentration ratio of the sample I ($\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$) from X-ray photoelectron spectroscopy (XPS) analysis.

Surface Atomic Concentration Ratio from XPS Analysis		
Si	Ge	O
32.0%	16.8%	51.2%

Table 3-2 Surface atomic concentration ratio of the sample I ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) from X-ray photoelectron spectroscopy (XPS) analysis.

Under $\pm 10V$ operation	$Si_{0.8}Ge_{0.2}O$	$Si_{0.5}Ge_{0.5}O$
STD	×	×
RTA 900°C 30s w/o PACO	×	×
RTA 900°C 30s with PACO	0.65V	2.8V
RTA 900°C 60s with PACO		3.1V

Table 3-3 Comparison of memory window under $\pm 10V$ sweeping operation with different samples and different treatment conditions.



Ge nanocrystals embedded in SiO_2 Memory	Memory window under $\pm 10V$:	Memory window after 10 years:
900°C 30s	2.8 V	0.36V (9.6%)
900°C 60s	3.1V	1.15V (25.5%)

Table 3-4 Comparison of memory window under $\pm 10V$ sweeping operation and remained charge ratio after 10 years with different thermal treatment time.

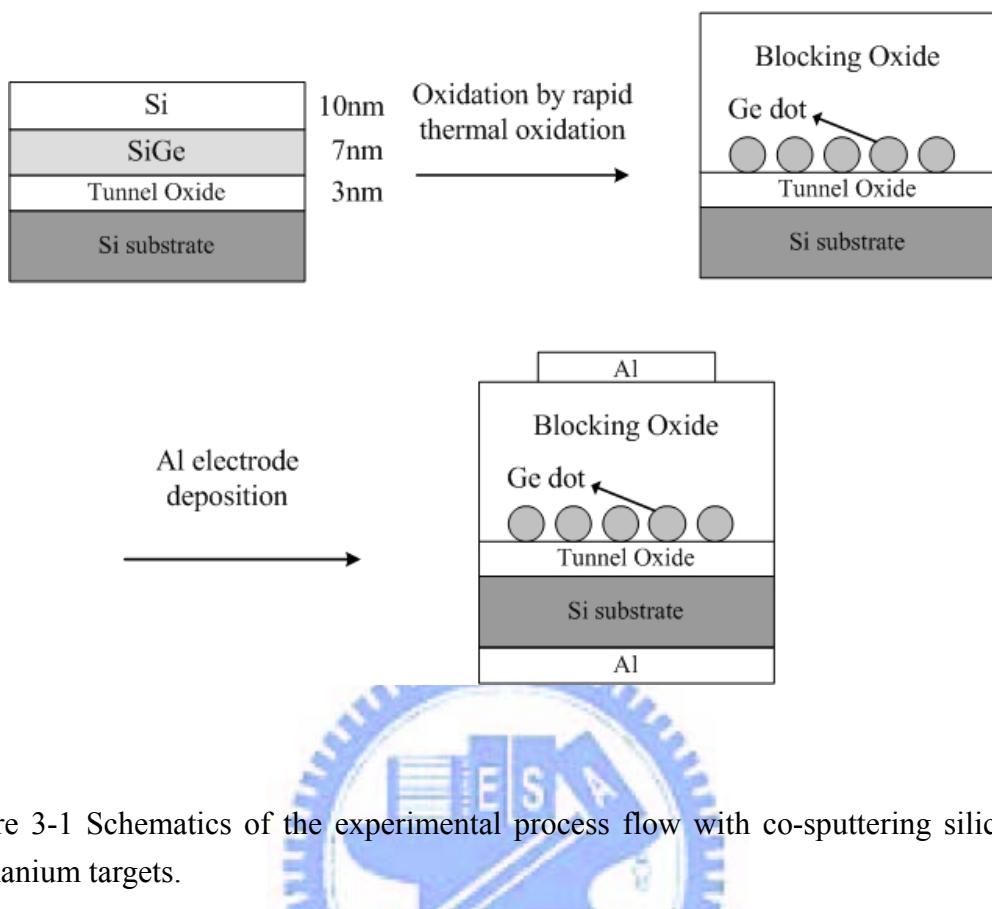


Figure 3-1 Schematics of the experimental process flow with co-sputtering silicon and germanium targets.

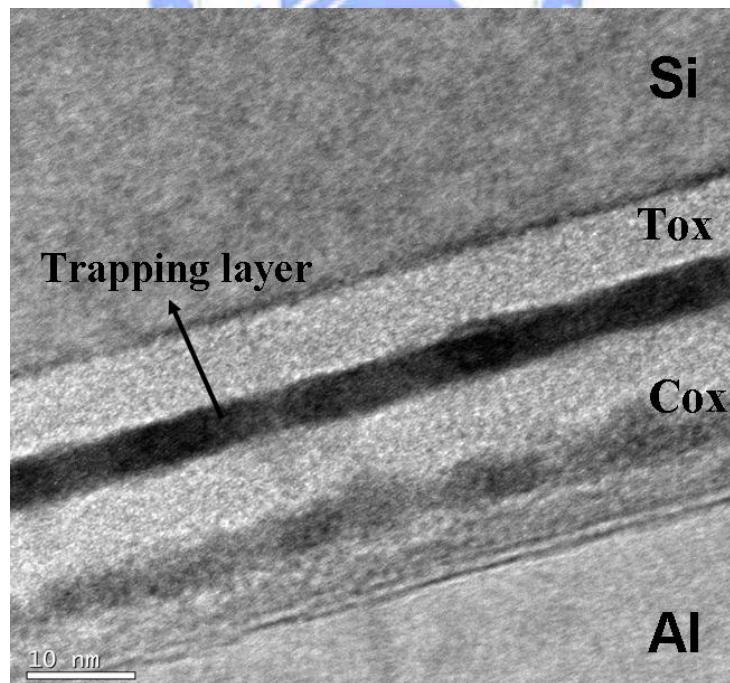


Figure 3-2 Cross-sectional TEM images of the MOIOS structure after a 900°C 60sec RTO process.

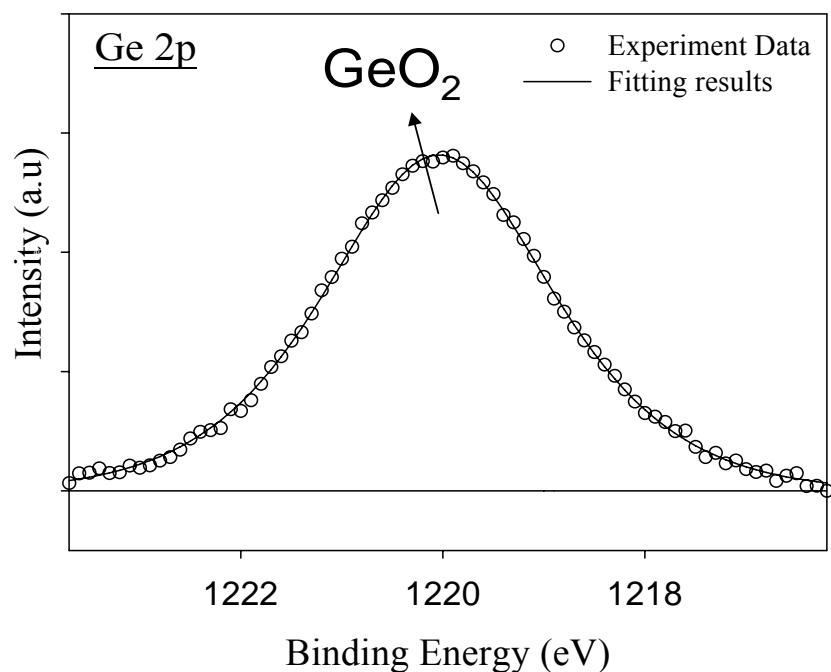


Figure 3-3 Ge 2p XPS analysis of the sample after 900°C 60sec RTO process. The peak position about 1220eV is the GeO₂ signal.

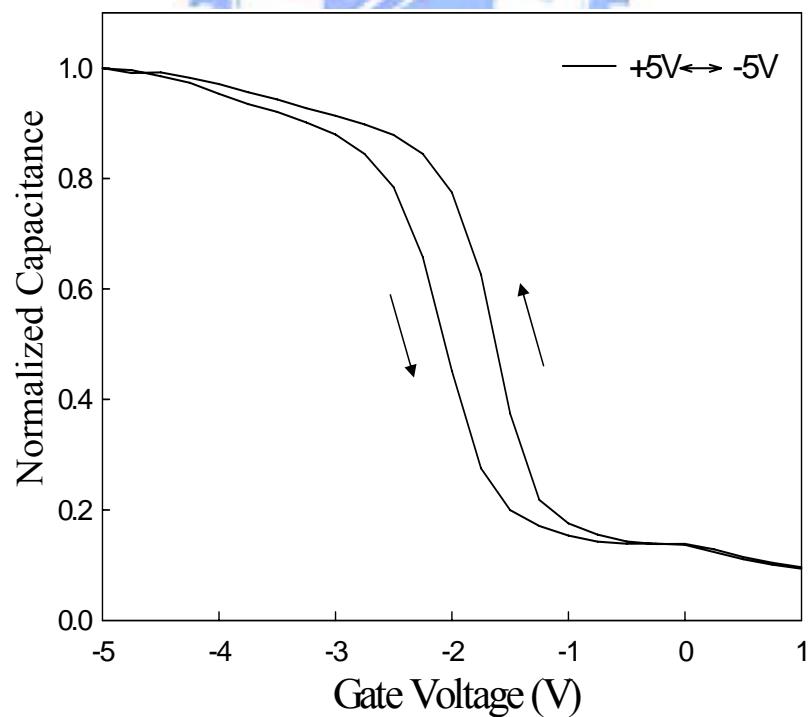


Figure 3-4 Capacitance-voltage (C-V) hysteresis of the fabricated MOIOS structure after a 900°C 60sec RTO process.

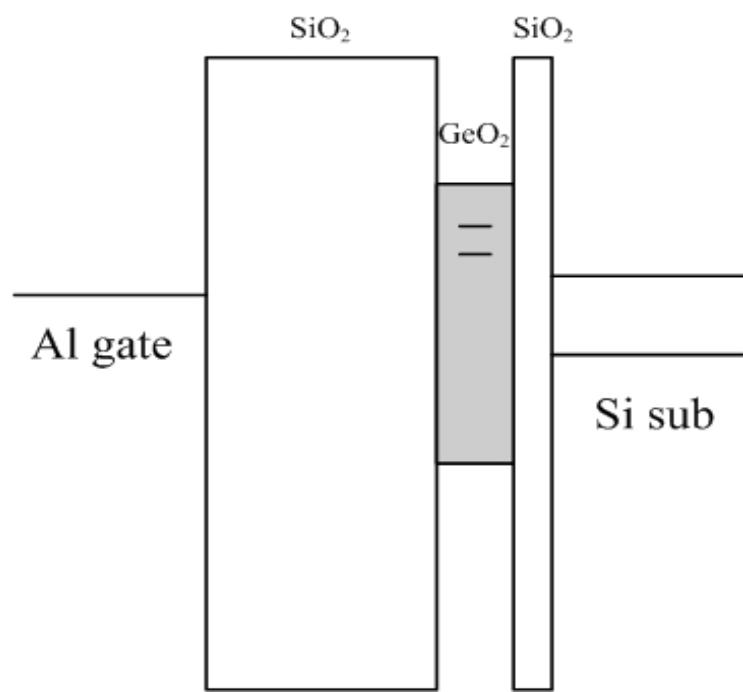


Figure 3-5 The band diagram for the charge trapping center for GeO_2 layer MOIOS structure.

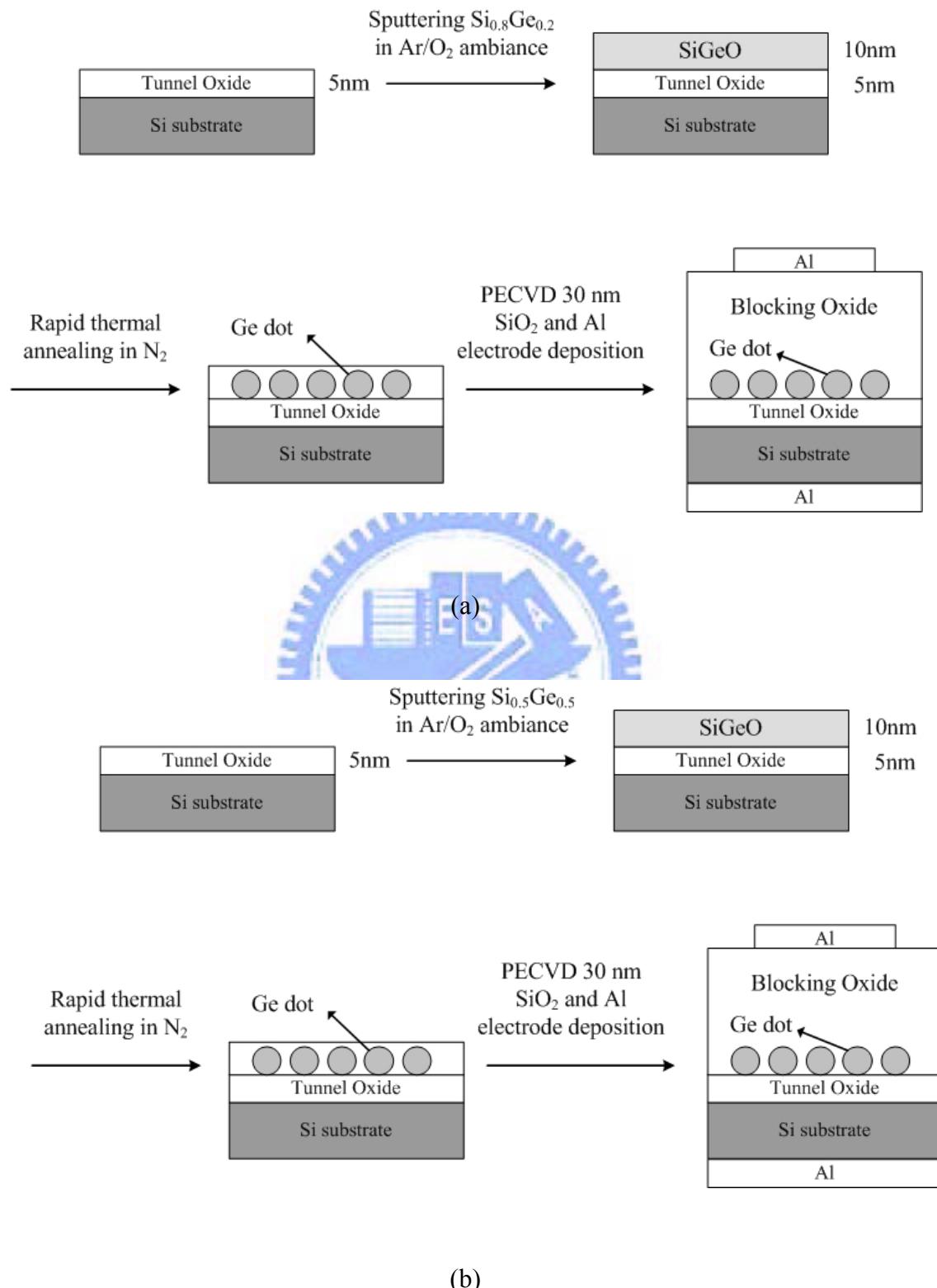


Figure 3-6 The process flow for different commixed target (a) $\text{Si}_{0.8}\text{Ge}_{0.2}$ (b) $\text{Si}_{0.5}\text{Ge}_{0.5}$ without pre-annealing capping oxide (PACO).

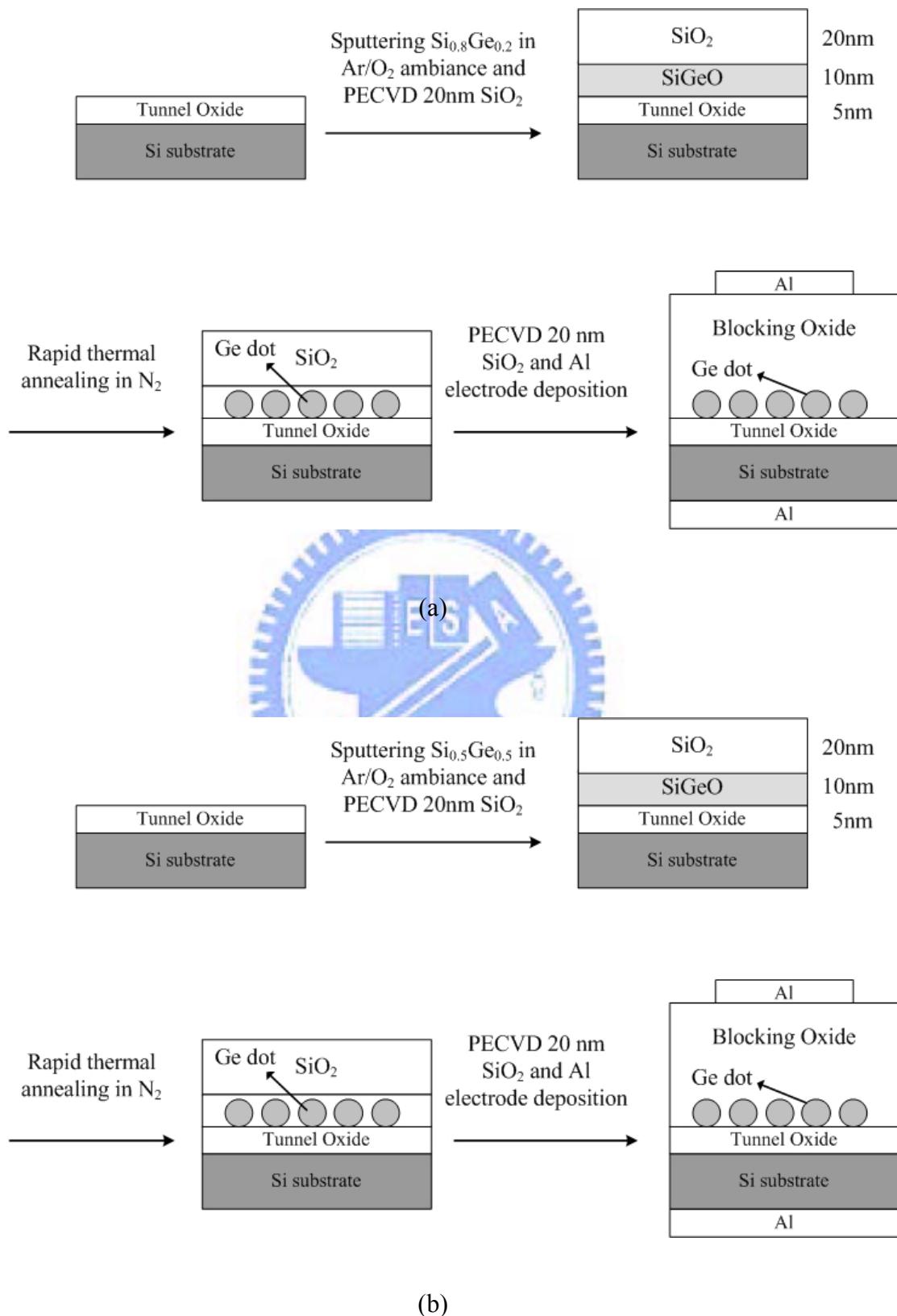


Figure 3-7 The process flow for different commixed d target (a) $\text{Si}_{0.8}\text{Ge}_{0.2}$ (b) $\text{Si}_{0.5}\text{Ge}_{0.5}$ with pre-annealing capping oxide (PACO) step.

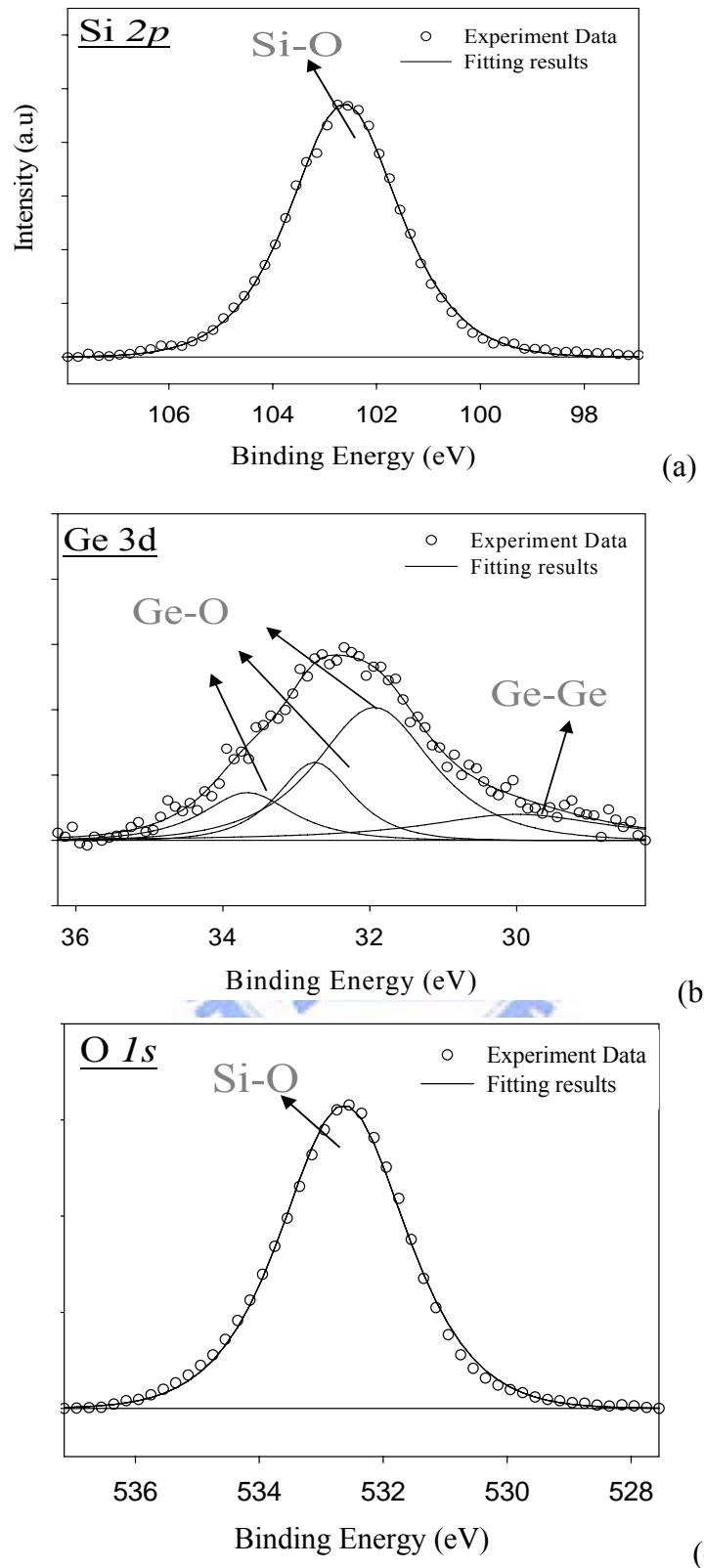


Figure 3-8 The XPS analysis by using an $Al\ K\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the sample I ($Si_{0.8}Ge_{0.2}O$) (a) Si 2p (b) Ge 3d (c) O 1s core-level spectra.

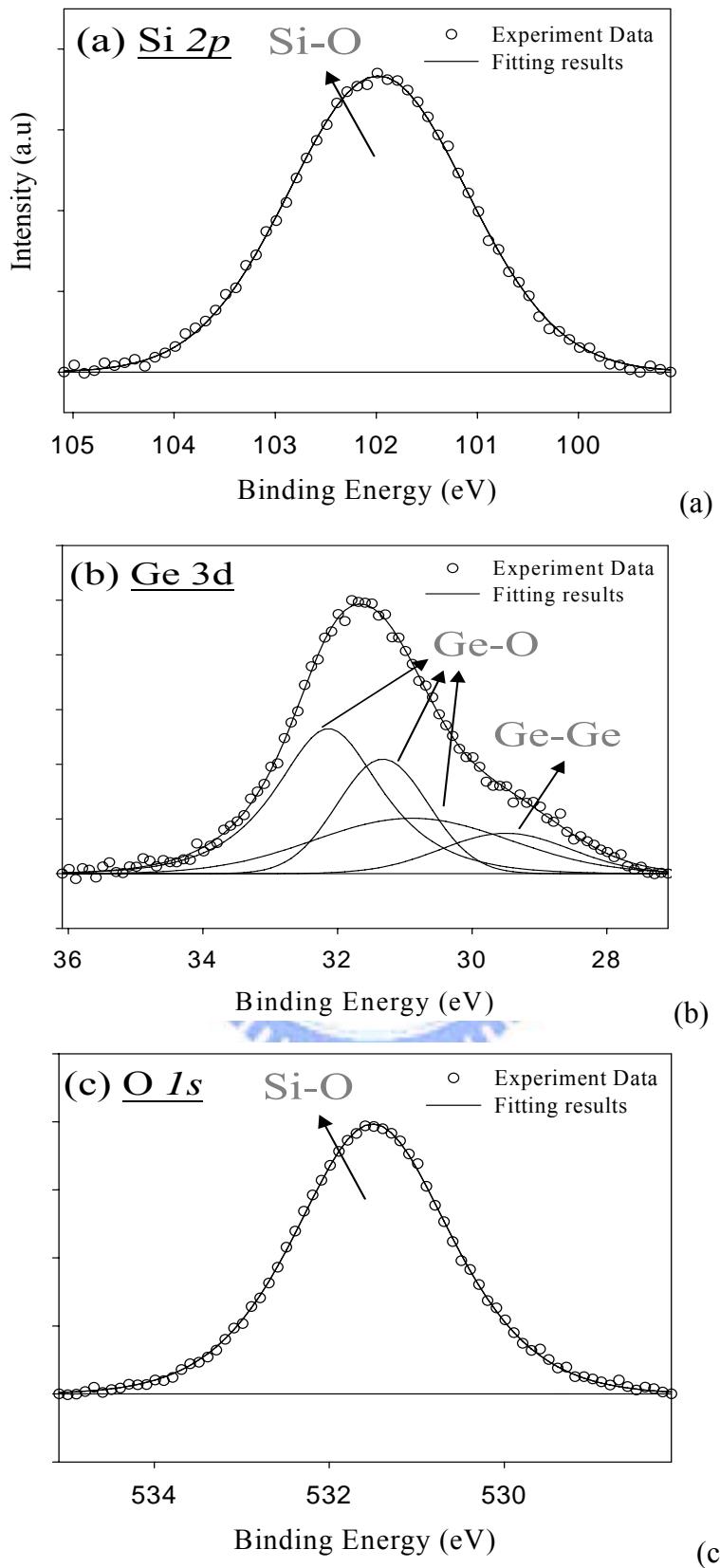


Figure 3-9 The XPS analysis by using an $Al\ K\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the sample II ($Si_{0.5}Ge_{0.5}O$) (a) Si 2p (b) Ge 3d (c) O 1s core-level spectra.

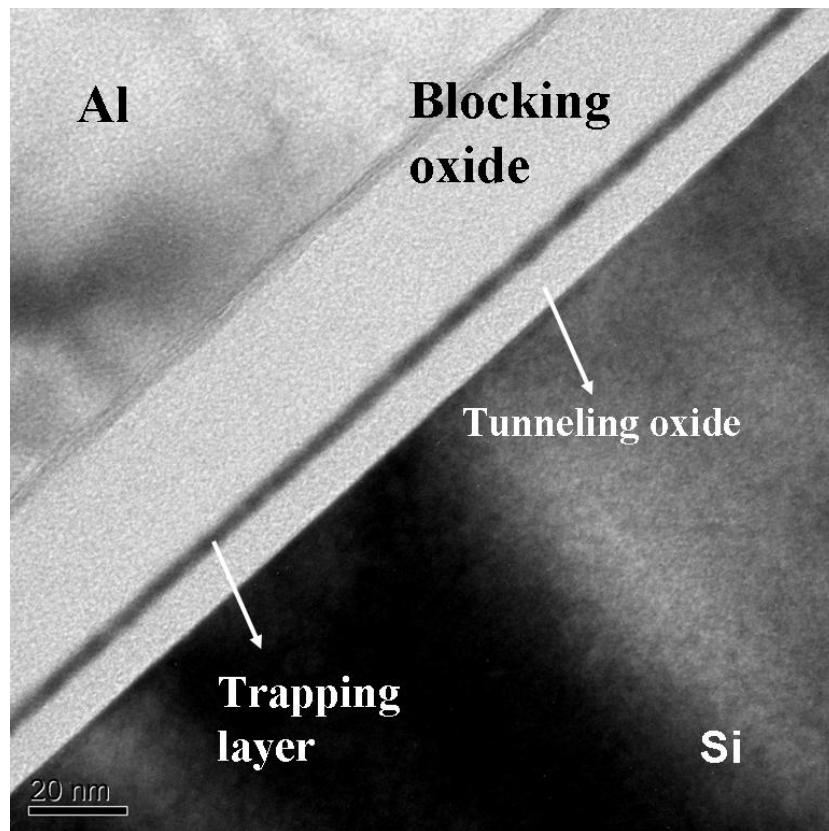
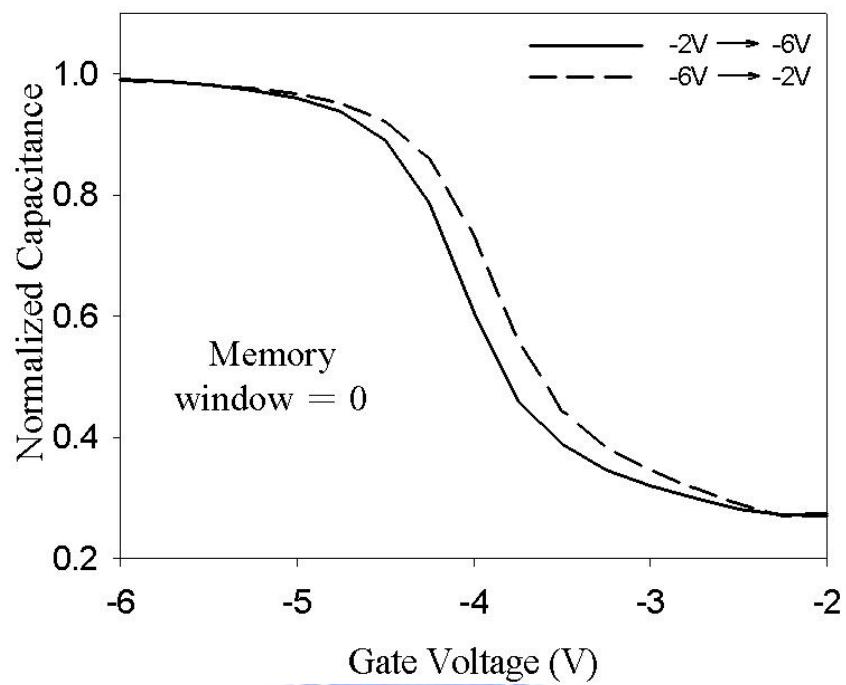
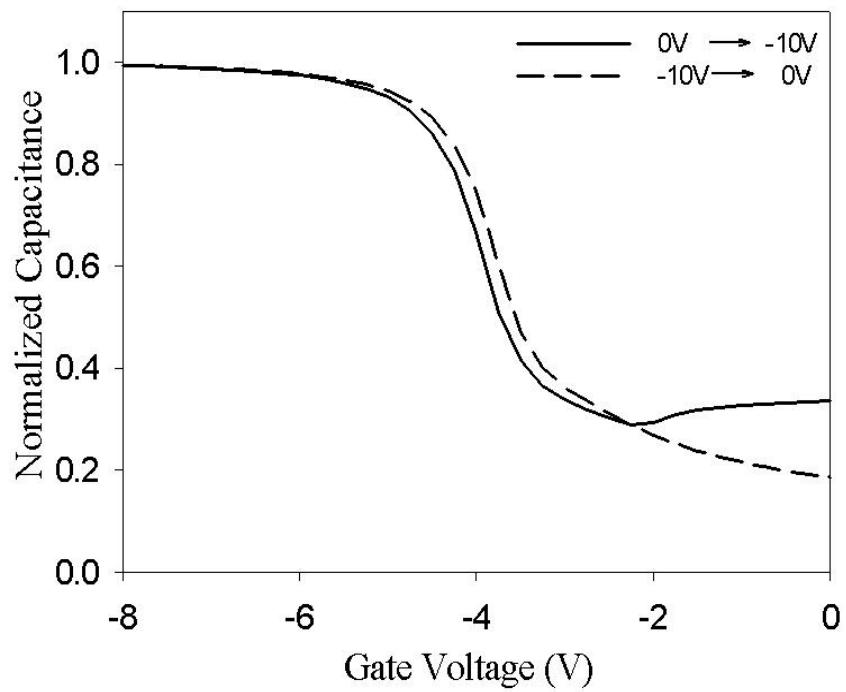


Figure 3-10 Cross-sectional TEM images of standard Sample II (Si_{0.5}Ge_{0.5}O) without any thermal treatment.



(a)



(b)

Figure 3-11 Capacitance-voltage (C-V) hysteresis of (a) standard sample I (b) standard sample II.

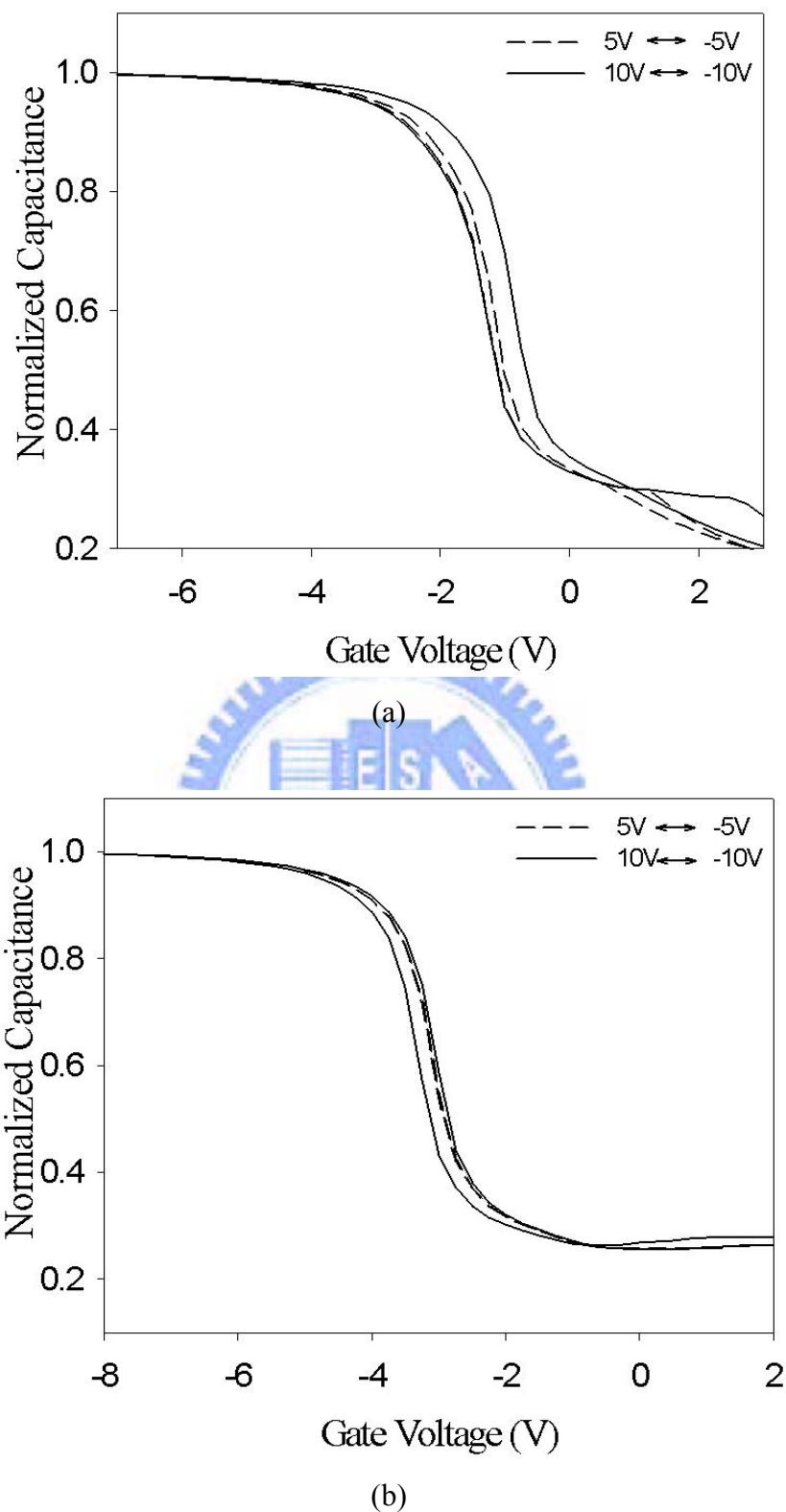


Figure 3-12 Capacitance-voltage (C-V) hysteresis of (a) sample I $\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$ (b) sample II $\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$ after RTA at 900°C for 30sec without PACO.

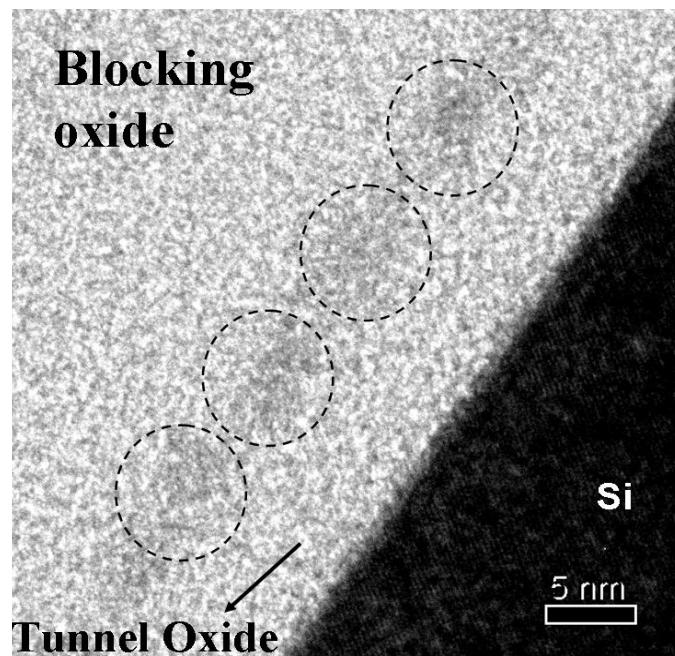


Figure 3-13 Cross-sectional TEM images of the Sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA at 900°C for 30sec without PACO.

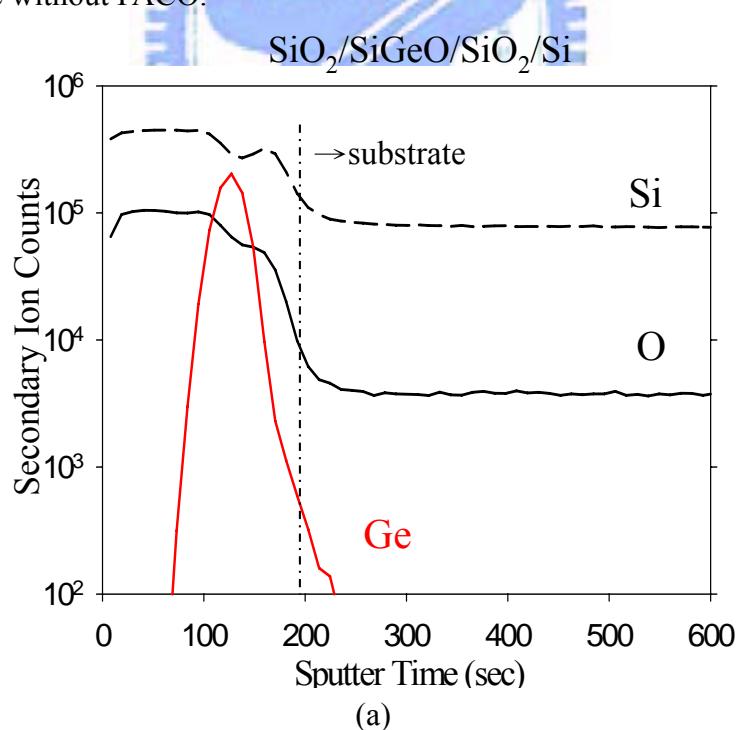
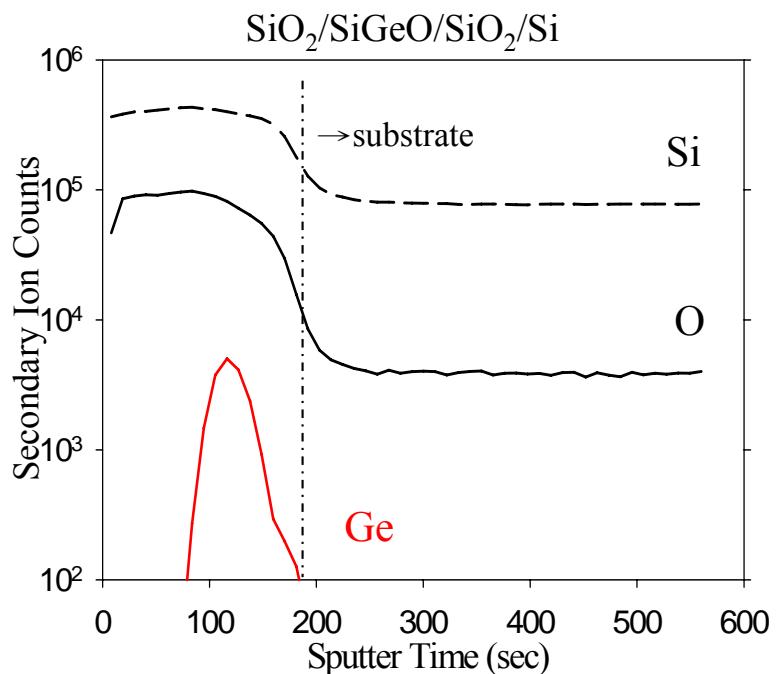
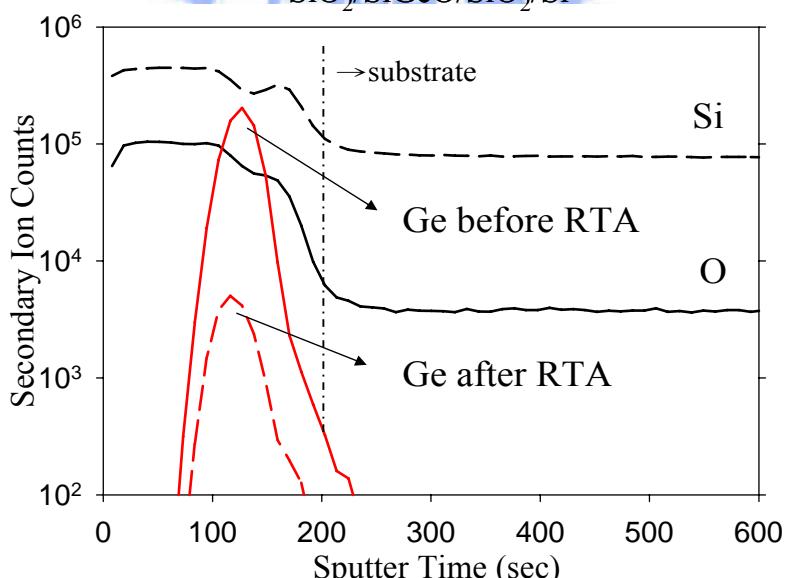


Figure 3-14 (a) SIMS depth profile of the standard sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$).



(b)



(c)

Figure 3-14 (b) SIMS depth profile of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA at 900°C for 30sec without PACO. (c) Comparison of the SIMS depth profile for the sample II with and without RTA treatment.

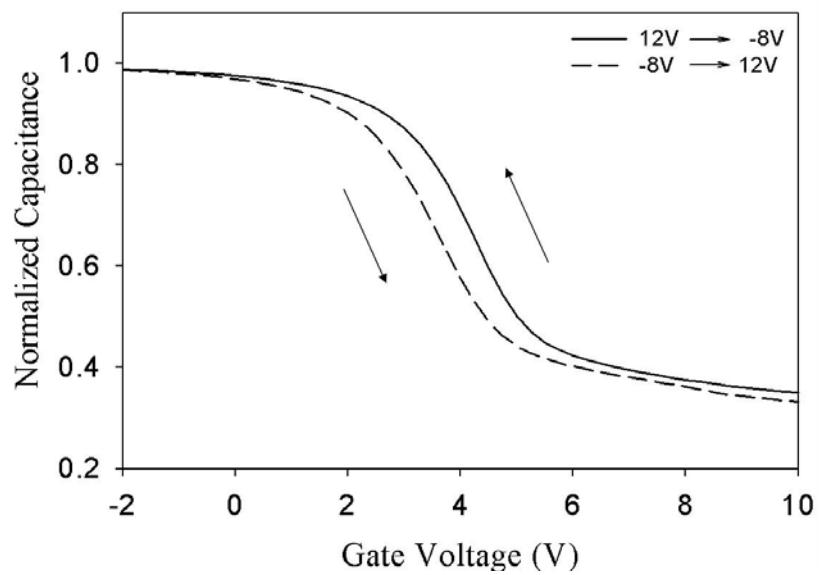


Figure 3-15 Capacitance-voltage (C-V) hysteresis of sample I $\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$ after RTA at 900°C for 30sec with PACO.

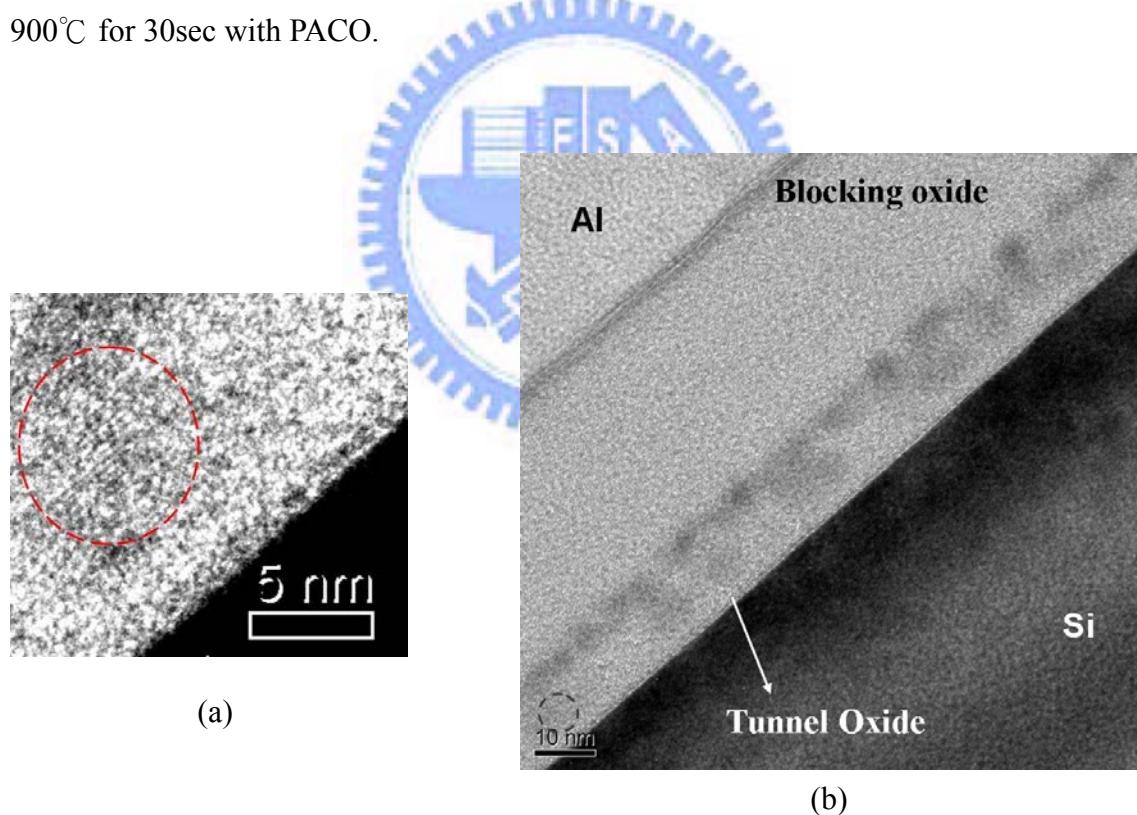


Figure 3-16 (a) and (b) TEM diagram of the sample I ($\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}$) after RTA at 900°C for 30sec with PACO.

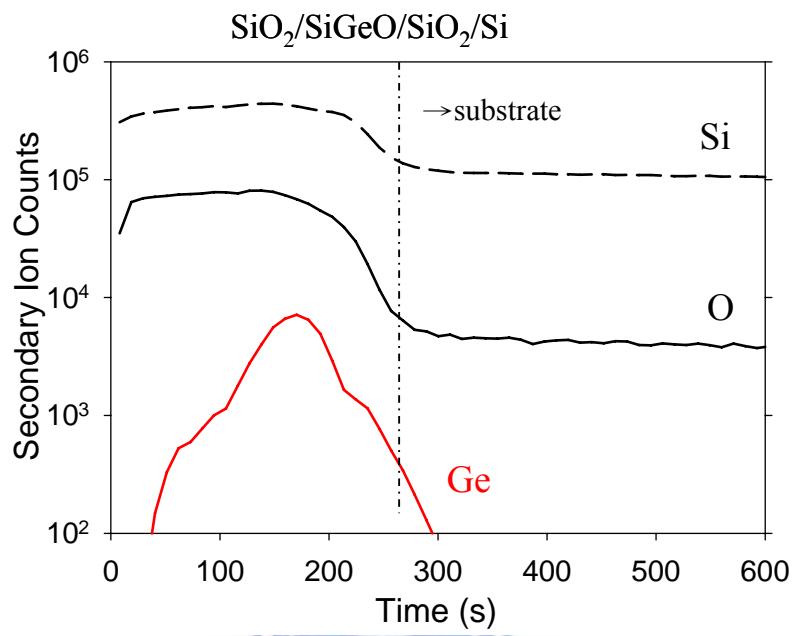


Figure 3-17 SIMS depth profile of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA at 900°C for 30sec with PACO.

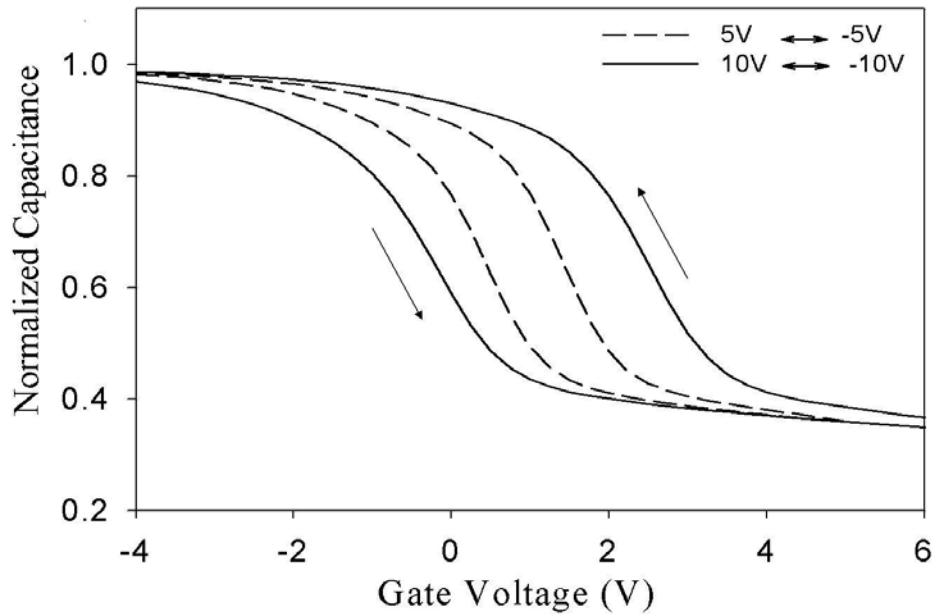


Figure 3-18 Capacitance-voltage (C-V) hysteresis of sample II $\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$ after RTA at 900°C for 30sec with PACO.

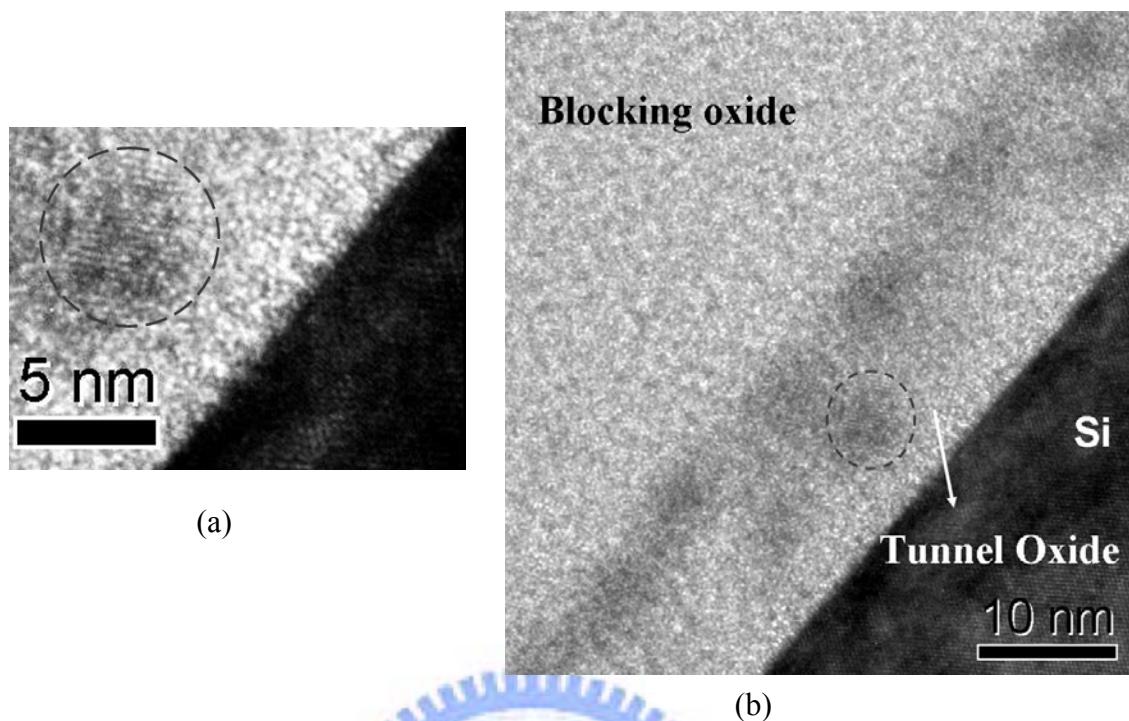


Figure 3-19 (a) and (b) TEM diagram of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA at 900°C for 30sec with PACO.

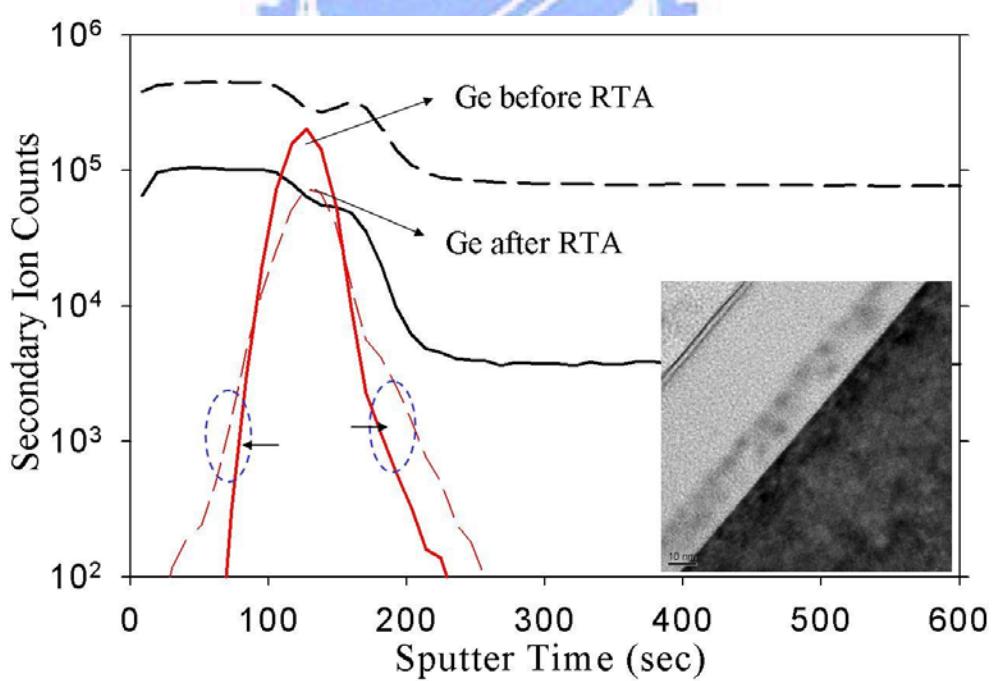


Figure 3-20 Comparison of the SIMS depth profile for the sample II before and after RTA at 900°C for 30sec with PACO.

(a)

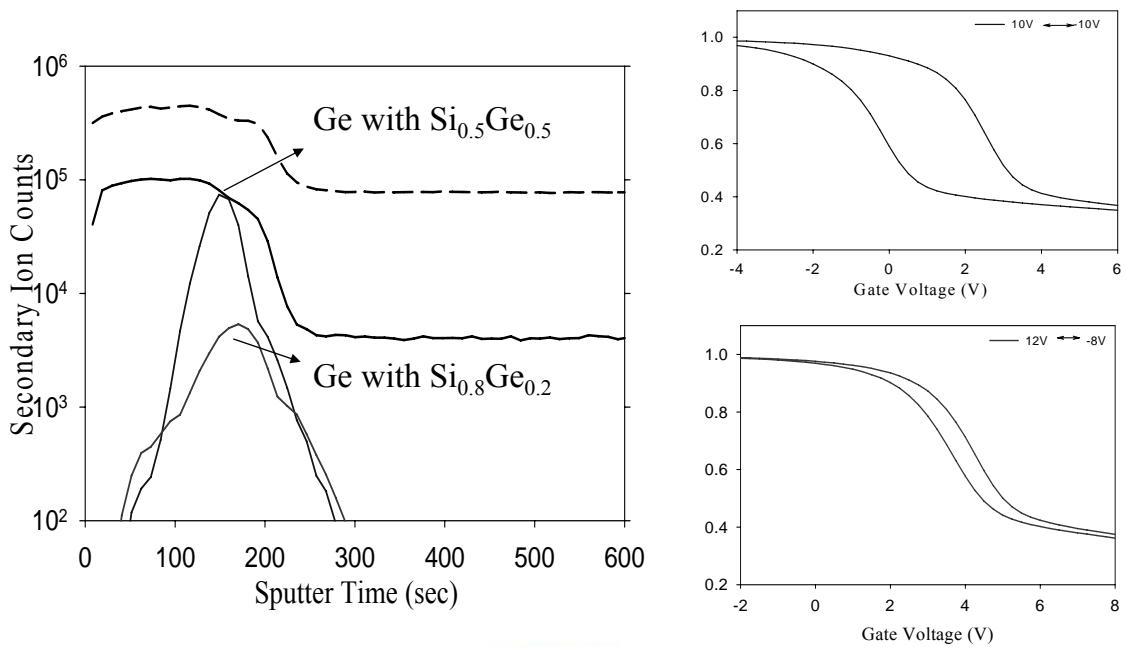


Figure 3-21 different sample I and sample II after RTA 900°C 30sec with PACO (a) comparison of SIMS depth profile (b) C-V curve of the sample II (c) C-V curve of the sample I.

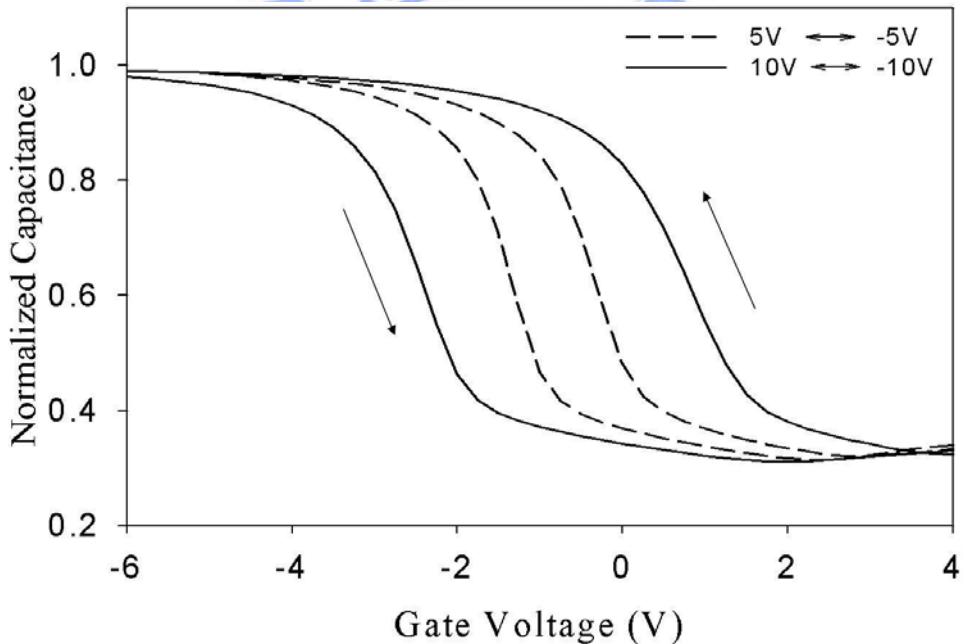


Figure 3-22 Capacitance-voltage (C-V) hysteresis of sample II $\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$ after RTA at 900°C for 60sec with PACO.

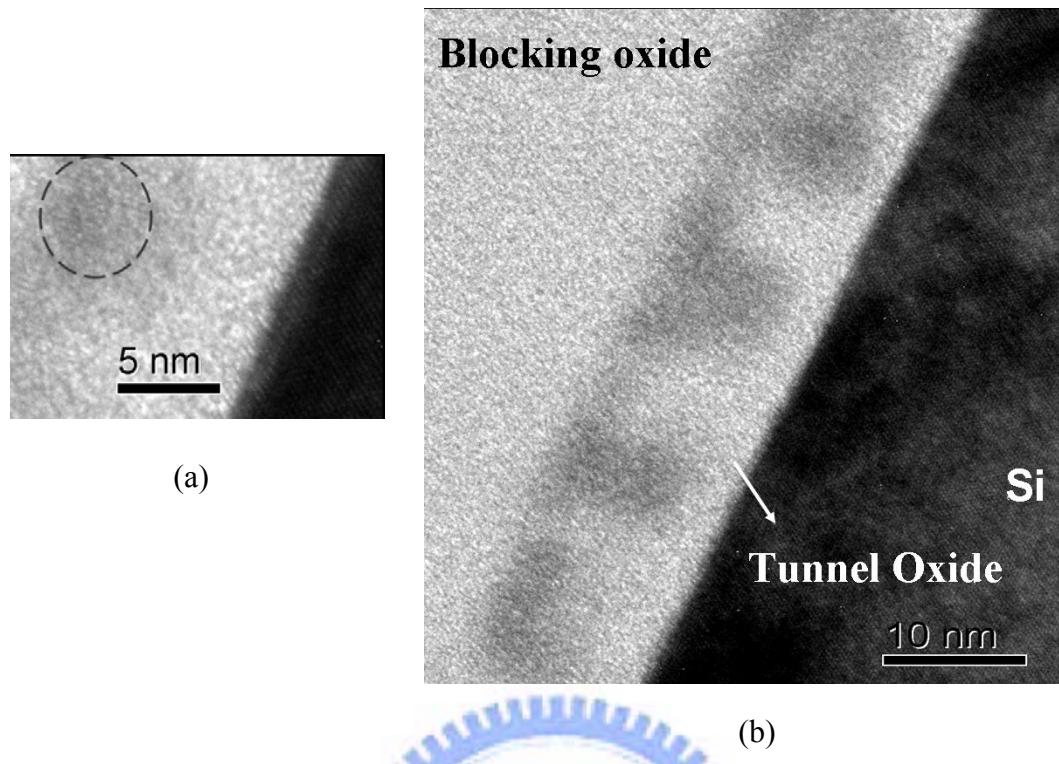


Figure 3-23 (a) and (b) TEM diagram of the sample II ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}$) after RTA at 900°C for 60sec with PACO.

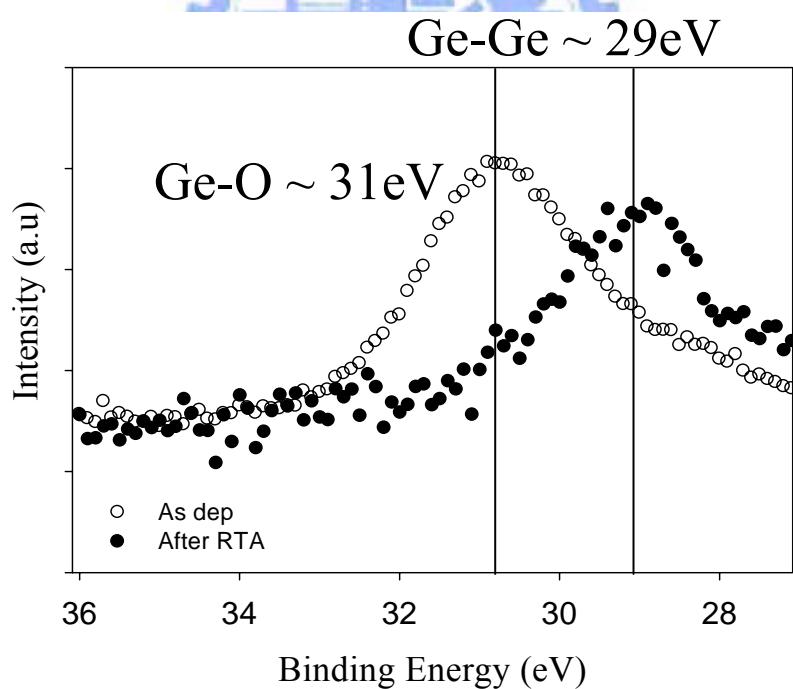
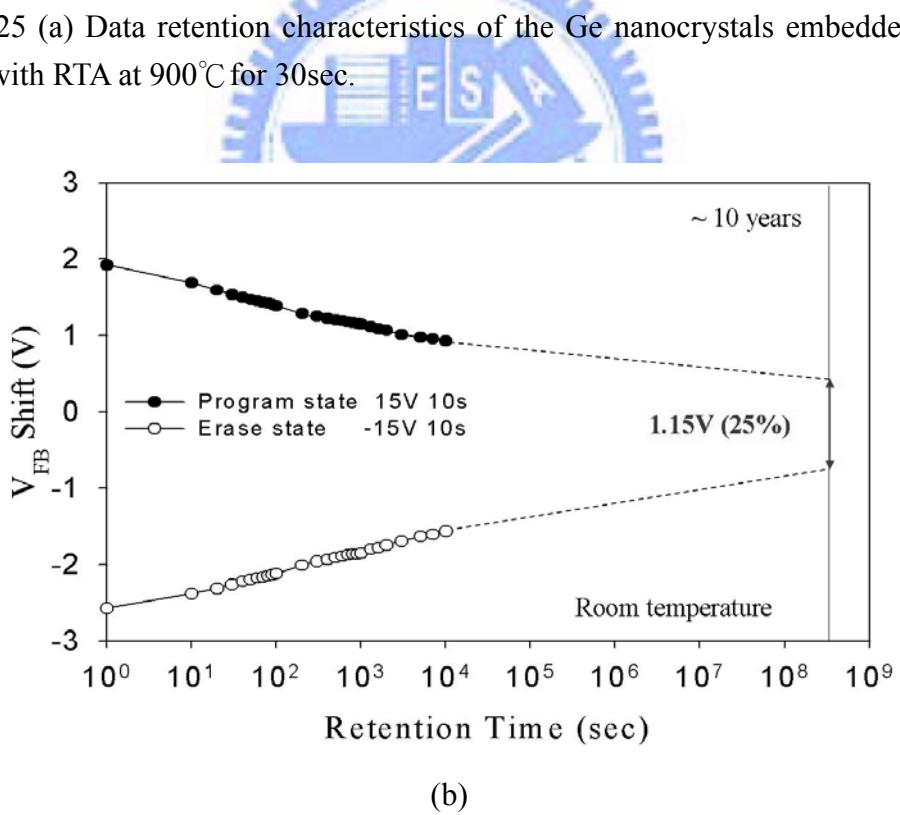
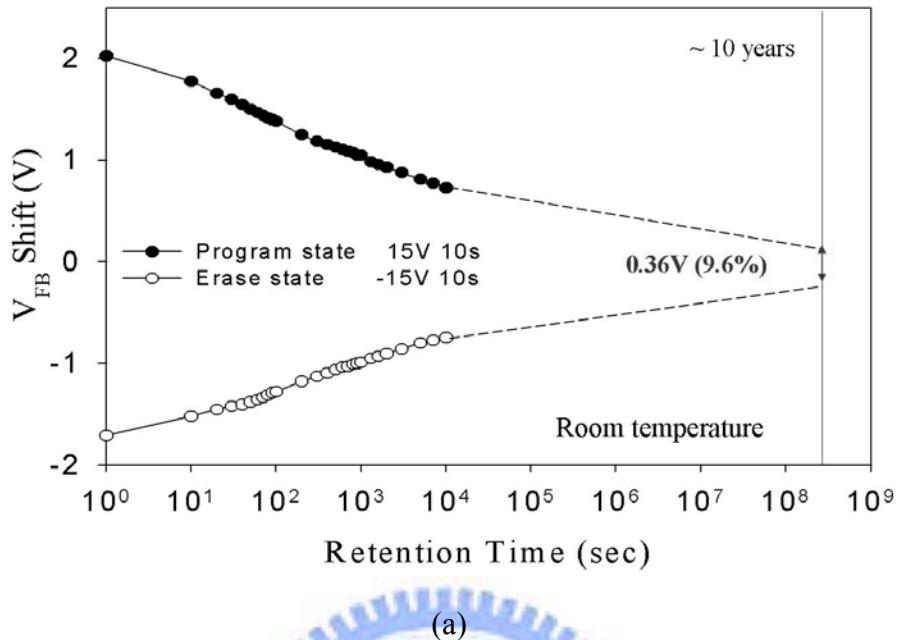


Figure 3-24 The X-ray photoelectron spectroscopy (XPS) analysis of the Ge 3d core-level spectrum. The Ge-O signal is at about 31 eV shift to lower bonding energy 29 eV which is the Ge-Ge signal peak position before thermal treatment (RTA).



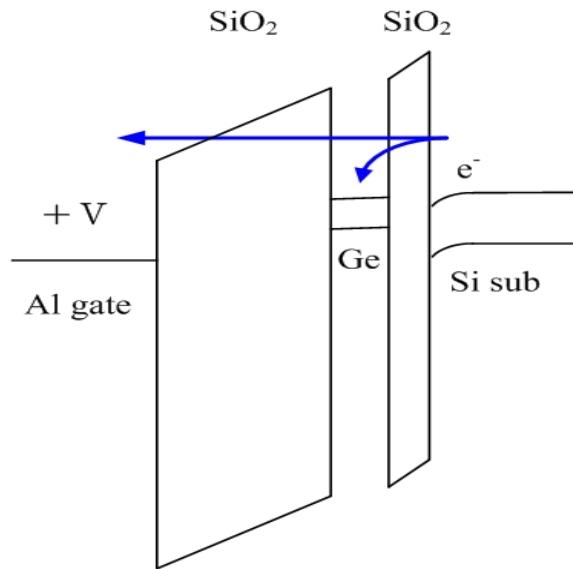


Figure 3-26 (a) The band diagram of the MOIOS structure as measuring current density-voltage (J-V) characteristics.

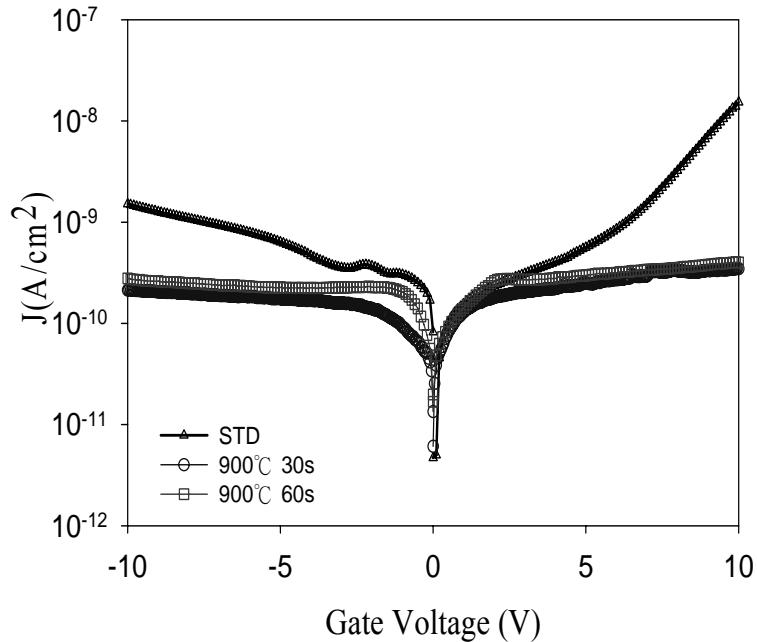
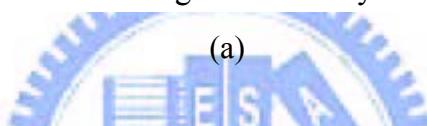
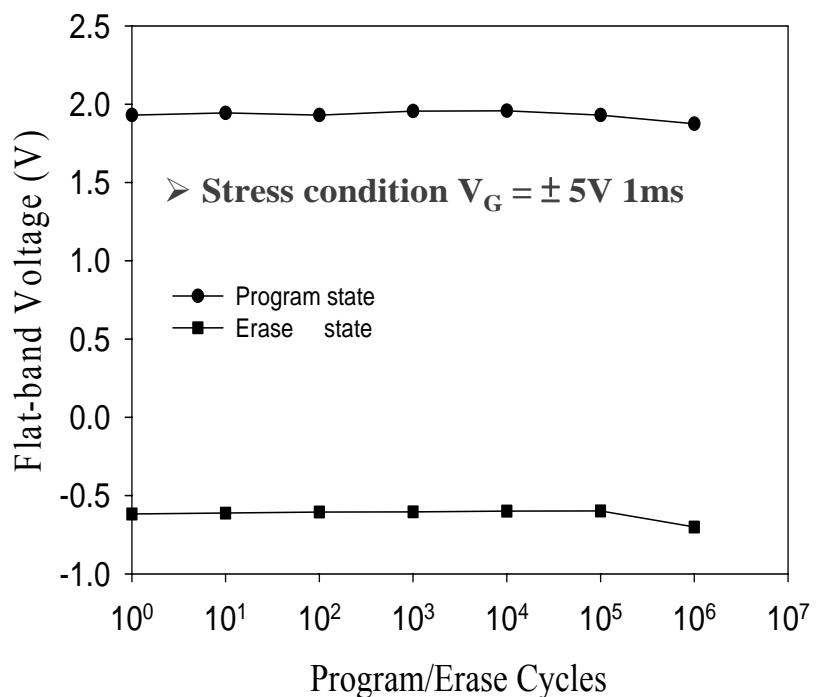
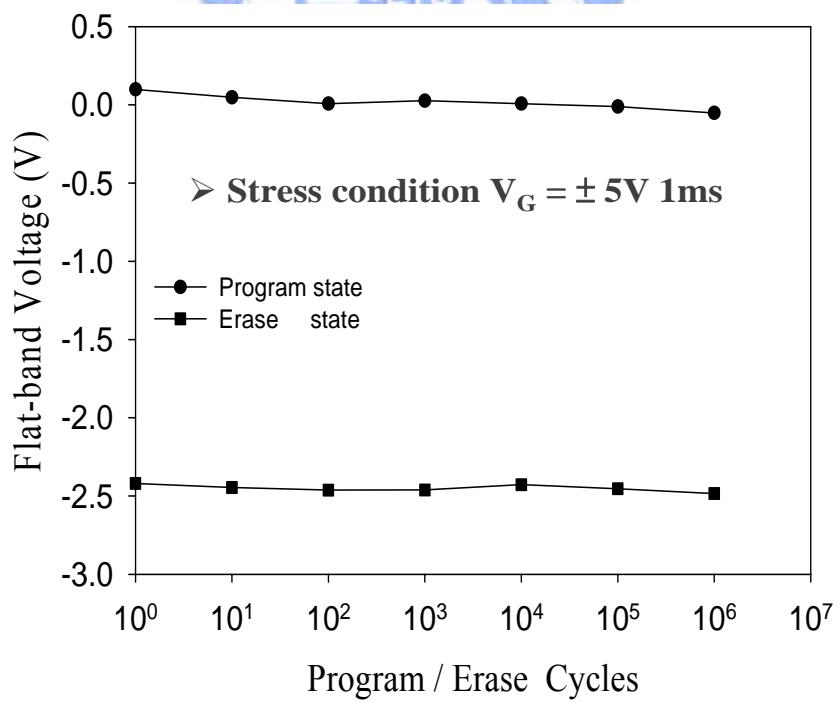


Figure 3-26 (b) The current density-voltage (J-V) of Ge nanocrystals embedded in SiO_x memory with and without thermal treatment (RTA).



(a)



(b)

Figure 3-27 Endurance characteristics of the Ge nanocrystal memory after RTA at (a) 900 °C for 30sec (b) 900°C for 60sec.

Chapter 4

Formation of Germanium Nanocrystals Embedded in Silicon Nitride Layer

4.1 Introduction

As we mentioned at the first chapter in the thesis, poly-si/oxide/nitride/oxide/silicon (SONOS) nonvolatile memory devices have been widely used in the integrated circuit market. The charge storage elements in SONOS memory are the charge traps distributed throughout the volume of the silicon nitride (Si_3N_4) layer. A typical trap has a density of the order 10^{18} - 10^{19} cm^{-3} according to Yang et al [4.1] and stores both electrons and holes (positive charge) injected from channel.

Base on the high trap density of silicon nitride, some study wad reported to fabricate germanium nanocrystal embedded in SiN_x dielectric [4.2]. The nitride can increase trapping states to improve memory window under electrical operation. Comparing to SONOS and Ge nanocrystals NVMs, a larger memory window can be obtained. When a memory device has a large memory window, it is easier to meet the requirement of 10 years.

In this chapter, we propose a new SiGeN film on tunnel oxide to form Ge nanocrystals embedded in SiN_x dielectric memory for nonvolatile memory.

4.2 Experimental Sample Preparation

Figure 4-1 indicates a schematic of experimental procedure. This nonvolatile memory-cell structure in this study was fabricated on a 4 inches p-type silicon (100) wafer, which had been removed native oxide and particles by RCA process. After a standard RCA clean, a 5-nm-thick tunnel oxide was thermally grown by a dry oxidation process at 950°C in an atmospheric pressure chemical vapor deposition (APCVD) furnace. Subsequently, a 8-nm-thick nitrogen incorporated $\text{Si}_{0.5}\text{Ge}_{0.5}$ (SiGeN) layer was deposited on tunnel oxide by reactive sputtering of $\text{Si}_{0.5}\text{Ge}_{0.5}$ commixed target in the Ar/N_2 (24sccm/20sccm) ambiance at room temperature. This step can obtain a nitrogen incorporated $\text{Si}_x\text{Ge}_{1-x}$ layer as a charge trapping layer in our memory. We choose the $\text{Si}_{0.5}\text{Ge}_{0.5}$ target for this experiment due to previously result. $\text{Si}_{0.5}\text{Ge}_{0.5}$ target can allow

enough Ge concentration in the deposited film.

In order to prevent the Ge interacting with the oxygen in the chamber result in GeO out-diffusion during RTA process. We deposited a 20-nm-thick PECVD oxide on the trapping layer before RTA. We called this step “pre-annealing-capping-oxide” (PACO). After that, we annealed the sample by RTA at 900°C for 30sec and 60sec in Nitrogen ambiance. The RTA process was performed to cause the self-assembled of Ge nanocrystal in the charge trapping layer. After RTA process, a 20-nm-thick blocking oxide was deposited by PECVD at 300°C. Al gate electrodes on back and front side of the sample were finally deposited and patterned to form a metal/oxide/insulator/oxide/silicon (MOIOS) structure. And we noted this MOIOS structure for “Sample III”.

Electrical characteristics, including the capacitance-voltage (C-V) hysteresis, current density-voltage (J-V), retention, and endurance characteristics, were also performed. The J-V and C-V characteristics were measured by Keithley 4200 and HP4284 Precision LCR Meter with high frequency 1 MHz. In addition, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) were adopted for the micro-structure analysis and chemical material analysis.

4.3 Results and discussion

The XPS analysis by using an Al $K\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the sample III ($Si_{0.5}Ge_{0.5}N$), as shown in figure 4-2. Figure 4-2 (a), (b), (c) show Si 2p, Ge 3d, N 1s core-level spectra. We can roughly define the trapping layer atomic composition of sample III by a common method using similar calculation as equation (3-2). The “I” means the peak intensity, and “S” the material sensitivity of the ESCA. And the atomic concentration with silicon, germanium and nitrogen of the charge trapping layer are 45.2%, 23.1%, and 31.7%, as table 4-1 shown. We can observe that nitrogen was successfully incorporated during sputter process in the Ar/N₂ ambiance.

Figure 4-3 shows the transmission electron microscope (TEM) diagram of the control $Si_{0.5}Ge_{0.5}N$ sample (sample III). We can figure out a continuous and uniform SiGeN film was deposited on the tunnel oxide.

Figure 4-4 shows the capacitance-voltage (C-V) hysteresis of control sample III (without any thermal treatment). It is found that the control samples show no memory effect.

Figure 4-5 exhibits the typical C-V hysteresis of sample III ($Si_{0.5}Ge_{0.5}N$) after RTA

at 900°C for 30sec obtained with gate voltage from inversion to accumulation and reversely. From the figure 4-5, it is obviously observed that the Flat-band voltage shift (memory window, ΔV_{FB}) is about 3.2V under $\pm 10V$ operation. The MOIOS structure with Ge nanocrystals embedded in SiN_x dielectric exhibits clear counterclockwise hysteresis by a flat-band voltage shift, indicating a significant memory effect. We consider that the charges could be stored in both Ge nanocrystals and SiN_x traps. And the counterclockwise hysteresis is due to injection of electrons from the deep inversion layer and discharge of electrons from the deep accumulation layer of silicon substrate. Moreover, the memory window of Ge nanocrystals embedded in SiN_x matrix is large enough to be defined logic “high” and “low” state.

Figure 4-6 shows a cross-sectional TEM image of the sample III after RTA at 900°C for 30sec with PACO in nitrogen ambience. From figure 4-6, we can figure out some Ge atom was self-assembled and separated in the SiN_x dielectric. The SiN_x can be used to improve charge storage ability for nonvolatile memory application [4.3]. Compare figure 4-6 with figure 4-3, the charge trapping layer was no longer a continuous film after RTA process. And the average diameter of the nanocrystals is approximately 6~8 nm and the area density of the nanocrystals is estimated to be about $1.12 \times 10^{12} \text{ cm}^{-2}$ by TEM analysis.

In order to improve the performance of Germanium nanocrystal memory, we extended the RTA process at 900°C from 30sec to 60sec. Figure 4-7 shows the forward and reverse sweep C-V hysteresis of the sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) after RTA at 900°C for 60sec in nitrogen ambience with PACO. The sweeping condition were operated (i) from -5V to 5V, and reversely, (ii) from -10V to 10V, and reversely. The flat-band voltage shift is about 3.75V under $\pm 10V$ gate sweeping operation. From the above results, we can figure out that the charging effect of Ge nanocrystals embedded SiN_x after longer RTA treatment is more significant.

Figure 4-8 show the TEM image of the sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) after RTA at 900°C for 60sec with PACO. From the figure 4-8, Ge was segregated and nucleated obviously. The average diameter of the nanocrystals is approximately 6-9 nm and the area density of the nanocrystals is estimated to be about $1.06 \times 10^{12} \text{ cm}^{-2}$ by TEM analysis. Compare figure 4-8 with figure 4-6, we can discover that the nucleation and isolation of Ge nanocrystals became better after longer thermal treatment. That is one the reasons for 900°C 60sec sample has larger memory window than the other one.

Mechanism of Germanium Nanocrystal Formation by Thermal Treatment:

From the section 3.4, we used chemical reaction free energy and Gibbs free energy

to explain the phenomena for Ge self-assembled in the SiGeO ternary dielectric film.

In this section, we will discuss the mechanism of Ge nanocrystals formation by thermal treatment. Si reacts preferentially with N due to the lower Gibbs free energy of the Si compound than Ge compound in the Si-Ge-N ternary system [4.4]. And then unreacted Ge atoms accumulated and nucleated. The similar phenomena were observed in Si-Ge-O system.

The reliability characteristics, such as retention time and endurance, were also discussed in this study. Note that the reliability measured samples be discussed later are all with the “PACO” condition.

The charge retention characteristics of the MOIOS structure with Ge nanocrystals embedded in the SiN_x after RTA at 900°C for 30sec and 60sec are illustrated in figure 4-9 (a) and (b). The retention measurements are performed at room temperature by operating a $\pm 15\text{V}$ gate voltage stress for 10 sec. The flat-band voltage shift is obtained by comparing the C-V curves from a charged state to the quasi-neutral state. When the carriers are stored in the nanocrystals, the stored charges will raise the nanocrystal potential energy and increase the probability of escaping from the nanocrystal to silicon substrate or gate. Figure 4-9 (a) shows retention time of the sample after RTA at 900°C for 30sec. The memory window decays during the stored charges leaked out from the nanocrystals to substrate or gate. And a 0.62 V memory window is expected to maintain after 10 years, which is approximately 16% of the stored charges retained in the nanocrystals. Figure 4-9 (b) shows retention time of the sample after RTA at 900°C for 60sec. Similarly, the memory window decays during the stored charges leaked out from the nanocrystals to substrate or gate. And a 1.22 V memory window is expected to maintain after 10 years, which is approximately 28% of the stored charges retained in the nanocrystals. Both of them retain a memory window larger than 0.5V, which is enough to define “1” or “0” of memory state. It is easily observed the sample with longer thermal treatment (RTA) condition shows better retention time. The explanation of the different results will be discussed later.

Endurance characteristics of the MOIOS structure with Ge nanocrystals embedded in the SiN_x with different RTA times are illustrated in figure 4-10 (a) and (b). Pulses ($V_G = \pm 5\text{V}$, 1ms) were applied to evaluate endurance characteristics for the Program/Erase operation. Both of the (a) 900°C for 30sec and (b) 900°C for 60sec still show a better endurance performance after 10^6 program/erase cycles. Form the endurance data, we can find out the tunnel oxide and the dielectric below nanocrystal have good quality of both

sample.

Figure 4-11 illustrates the current density-voltage (J-V) characteristics of the MOISO structure with different thermal treatment time. The leakage current density in the figure 4-11 diagram decreases from 10^{-8} order to 10^{-9} with longer annealing time from 30sec to 60 sec. It means the quality of the blocking oxide and SiN_x dielectric above the Ge nanocrystals is getting better after longer RTA process.

For the endurance, current density-voltage (J-V) measurements and the TEM images, we can observe that both isolation of the Ge nanocrystals and the upper leakage path through blocking oxide affect the data retention characteristics.

The comparisons of memory window under $\pm 10\text{V}$ sweeping operation and memory window after 10 years of Ge nanocrystal embedded in SiN_x MOIOS structure between different thermal treatment (RTA) times were listed in Table 4-2. The 900°C 60sec sample shows larger memory window the 30sec one. That is because the longer thermal treatment induces the better isolation and nucleation of Ge. And longer thermal treatments not only make Ge isolated and nucleated better, but also reduce the SiN_x defects above the Ge NCs.

Let's compare the two different structures for Ge nanocrystals memory. All the results were done with PACO step. Table 4-3 shows the memory windows under $\pm 10\text{V}$ operation with different MOISO structure. Figure 4-12 (a) and (b) illustrate the energy band diagram of two different Ge nanocrystals structure, (a) for Ge nanocrystals embedded in SiO_x and (b) for Ge nanocrystals embedded in SiN_x . For the first structure, we can find out that Ge-rich samples show better electrical performance due to sufficient Ge atoms to form nanocrystal. From figure 4-12, we can observe that the charge trap centers of the second structure are not only (i) interface state between nanocrystals and the surrounding dielectric, (ii) nanocrystal confined state but also (iii) traps in side the SiN_x dielectric layer. Because the SiN_x supply additional accessible charge trap states, the second structure shows larger memory window than first one. We can say that the second structure is combined nanocrystal with SONOS structure.

4.4 Summary II

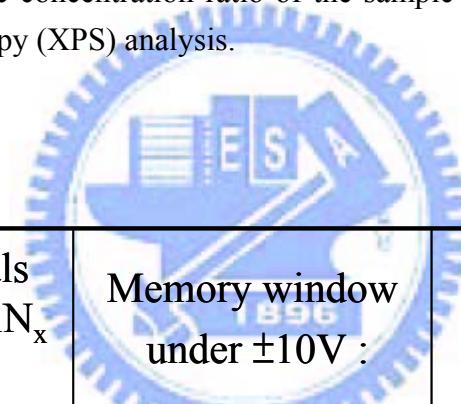
From the above experiments result, we successfully incorporated nitrogen into SiGe forming a new dielectric SiGeN film by sputtering a commixed $\text{Si}_{0.5}\text{Ge}_{0.5}$ target in an Ar/N_2 environment at room temperature. The self-assembled phenomenon of Germanium nanocrystal can be explained by the Gibbs free energy [4.4]. The Ge nanocrystals

embedded in SiN_x memory was fabricated easily. And the high density ($\sim 10^{12}$) of Ge nanocrystals can be achieved in this study. We observed that longer thermal treatment (RTA) can improve the isolation and nucleation of Ge nanocrystals. The memory window of RTA at 900°C for 30sec, 60sec conditions are 3.2V, 3.75V under $\pm 10\text{V}$ sweeping operation. Hence, the memory window is large enough to define high and low states for nonvolatile memory application. And Ge nanocrystals embedded in SiN_x shows better electrical characteristics than Ge nanocrystals embedded in SiO_x in the table 4-3. And the retention and endurance characteristics of the Ge nanocrystals embedded in SiN_x memory are good enough to be maintained after 10 years and 10^6 program/erase cycles. Finally, this novel and simple fabrication technique of germanium nanocrystals could be compatible with current manufacture process of the integrated circuit manufacture.



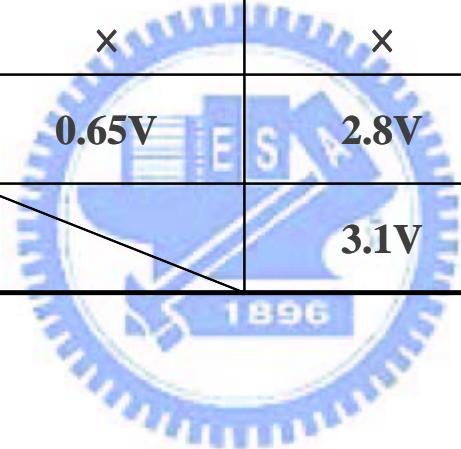
Surface Atomic Concentration Ratio from XPS Analysis		
Si	Ge	N
45.2%	23.1%	31.7%

Table 4-1 Surface atomic concentration ratio of the sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) from X-ray photoelectron spectroscopy (XPS) analysis.



Ge nanocrystals embedded in SiN_x Memory	Memory window under $\pm 10\text{V}$:	Memory window after 10 years:
900°C 30s	3.2 V	0.62V (16%)
900°C 60s	3.75V	1.22V (28%)

Table 4-2 Comparison of memory window under $\pm 10\text{V}$ sweeping operation and remained charge ratio after 10 years with different thermal treatment conditions.



Memory window under $\pm 10V$	Ge NCs embedded in SiO_x (Ge - poor)	Ge NCs embedded in SiO_x (Ge - rich)	Ge NCs embedded in SiN_x
STD	×	×	×
RTA 900°C 30s	0.65V	2.8V	3.2V
RTA 900°C 60s		3.1V	3.75V

Table 4-3 Comparison of memory window under $\pm 10V$ sweeping operation with different samples and different treatment conditions.

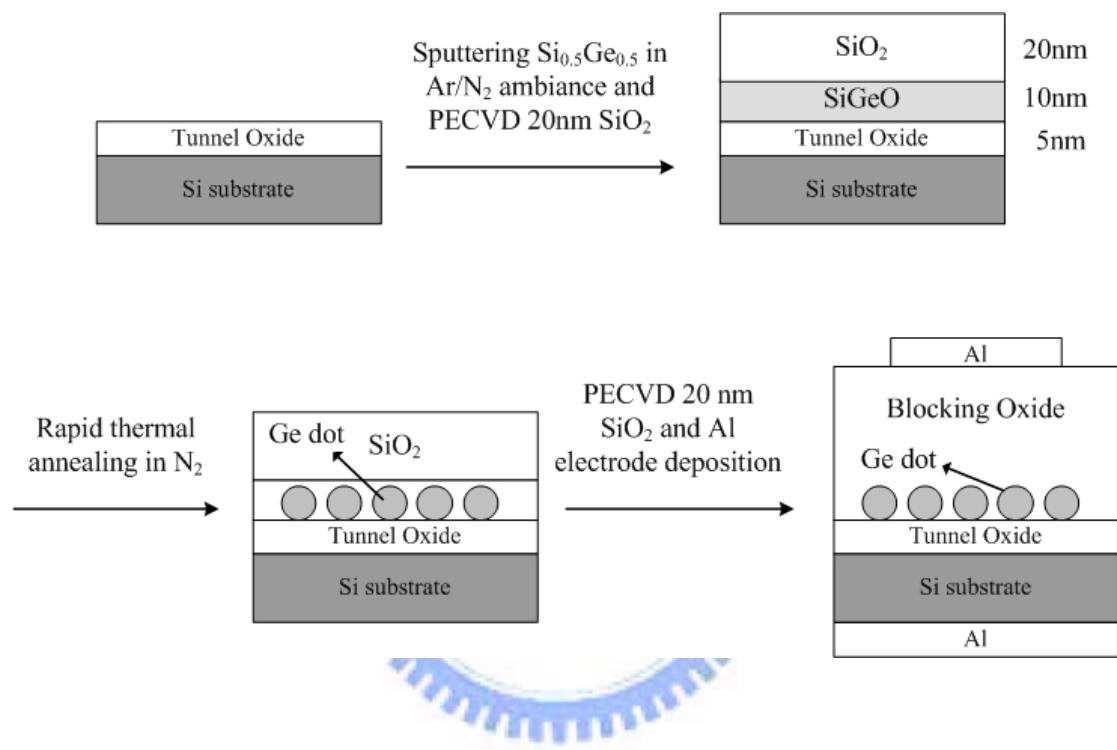


Figure 4-1 The process flow for sputtering $\text{Si}_{0.5}\text{Ge}_{0.5}$ commixed target in Ar/N₂ ambience with pre-annealing capping oxide (PACO) step.

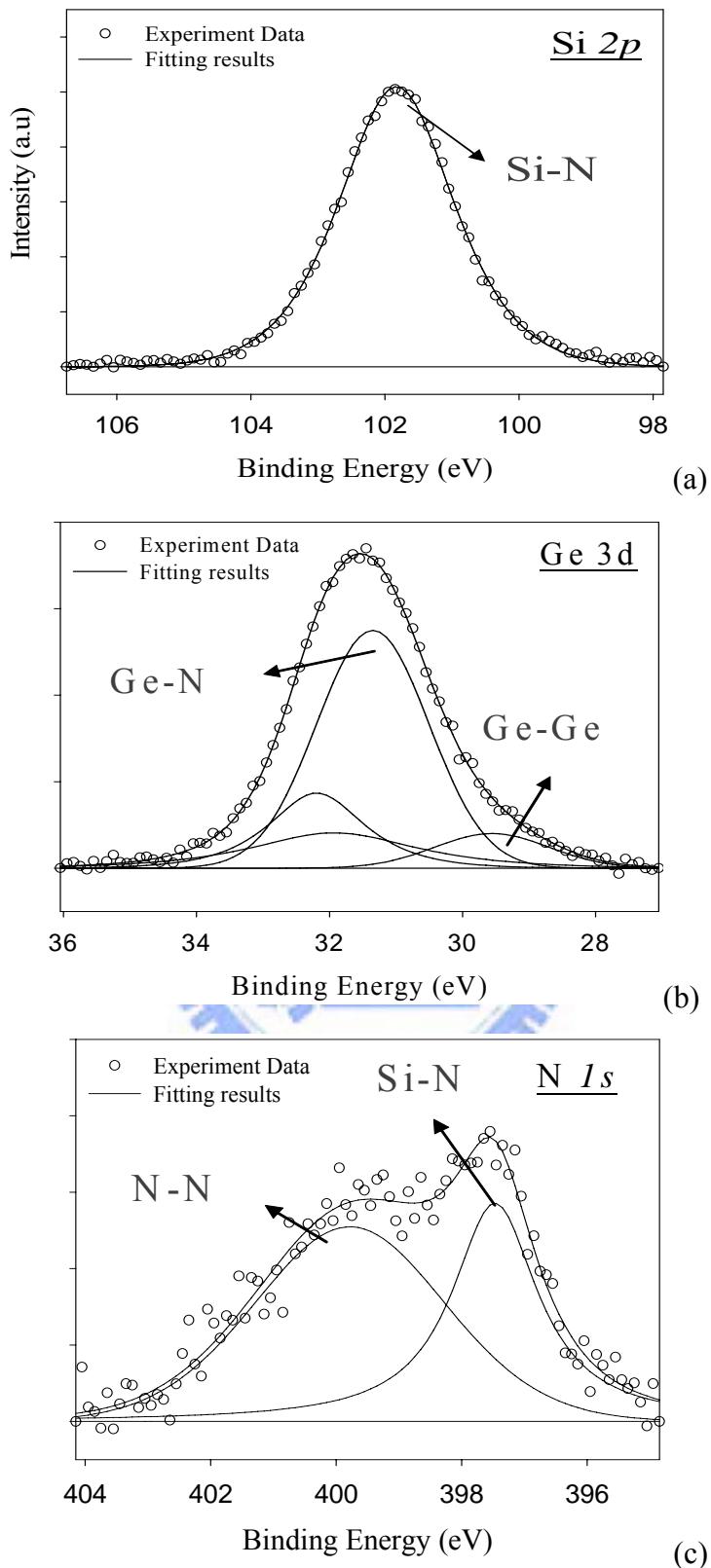


Figure 4-2 The XPS analysis by using an $Al\ K\alpha$ (1486.6 eV) x-ray radiation is demonstrated the chemical composition of the sample III ($Si_{0.5}Ge_{0.5}N$) (a) Si 2p (b) Ge 3d (c) N 1s core-level spectra.

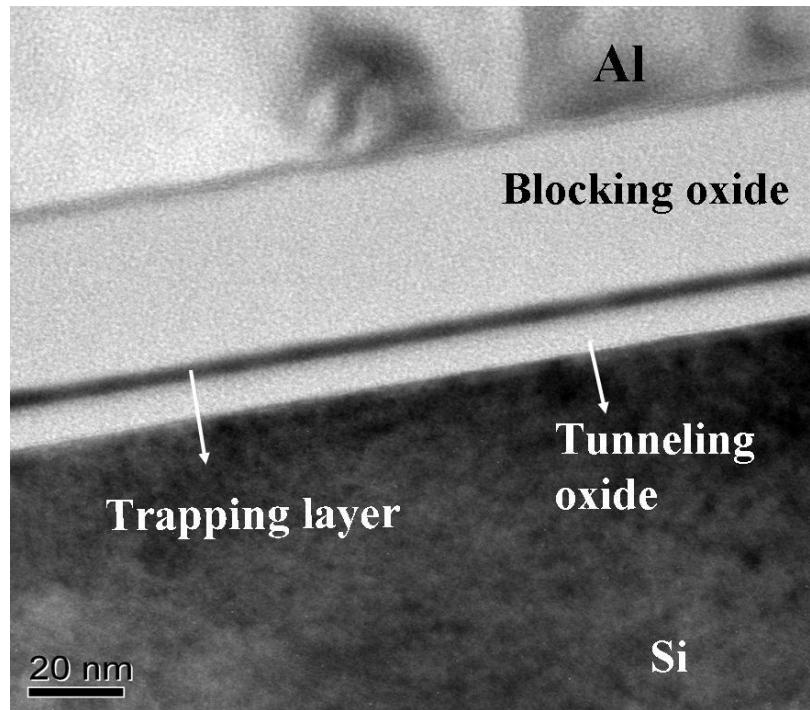


Figure 4-3 Cross-sectional TEM images of standard Sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) without any thermal treatment.

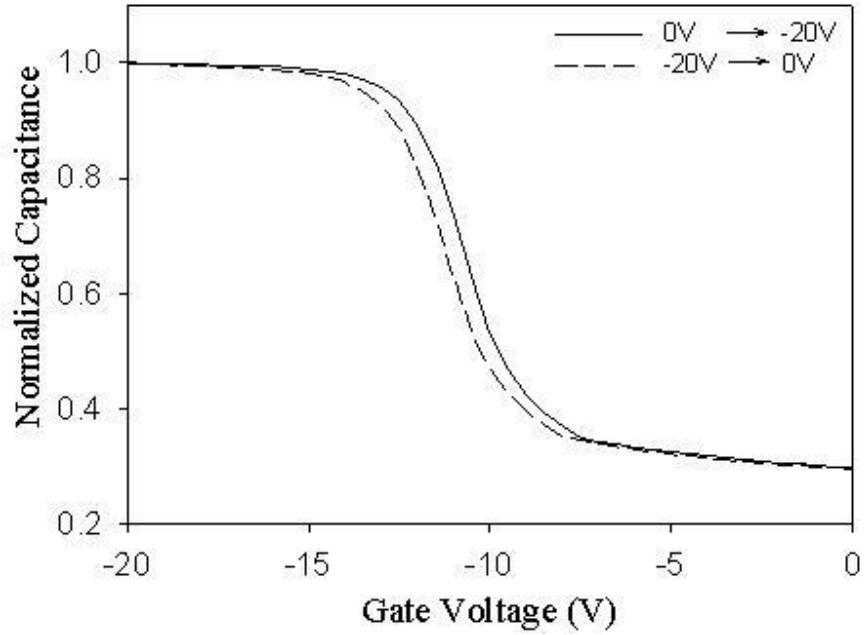


Figure 4-4 Capacitance-voltage (C-V) hysteresis of standard sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) without any thermal treatment.

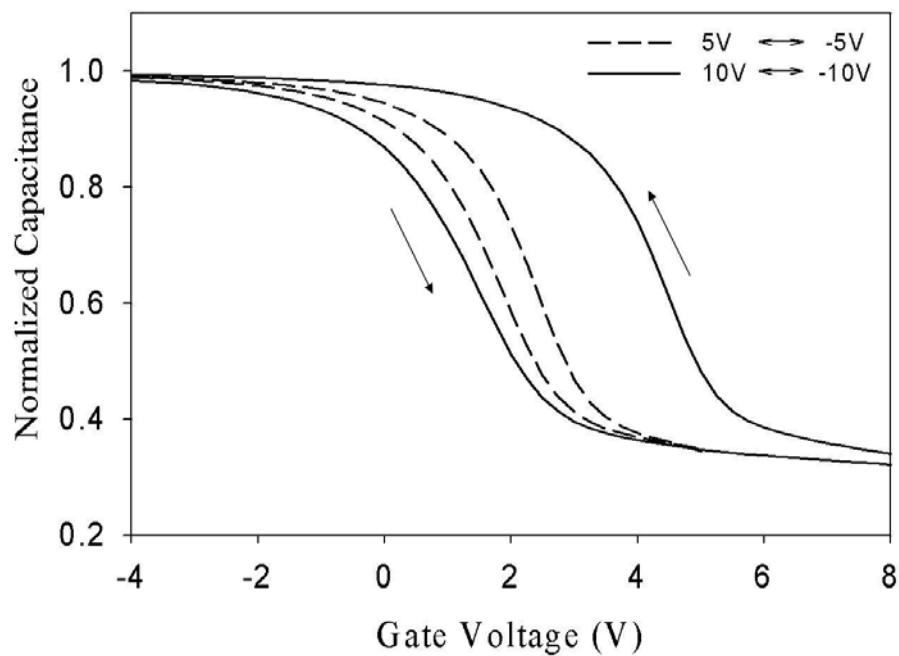


Figure 4-5 Capacitance-voltage (C-V) hysteresis of sample III $\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$ after RTA at 900°C for 30sec with PACO.

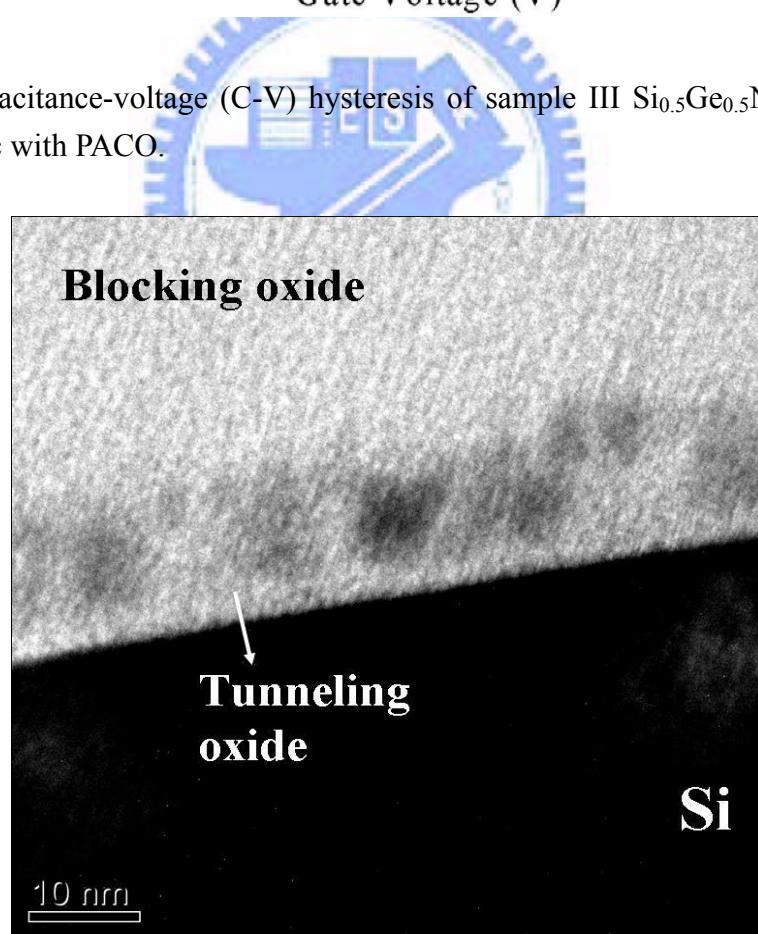


Figure 4-6 TEM diagram of the sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) after RTA at 900°C for 30sec with PACO.

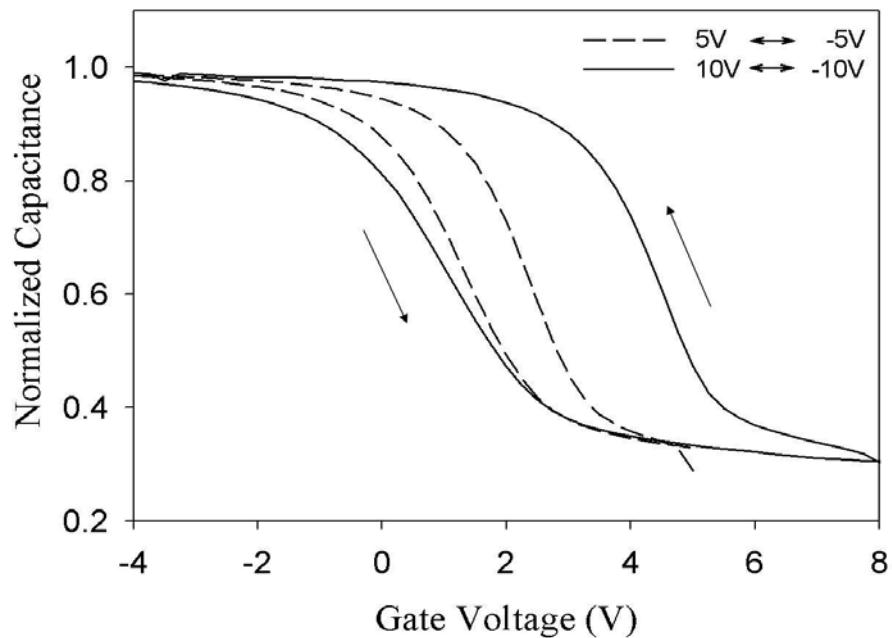


Figure 4-7 Capacitance-voltage (C-V) hysteresis of sample III $\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$ after RTA at 900°C for 60sec with PACO.

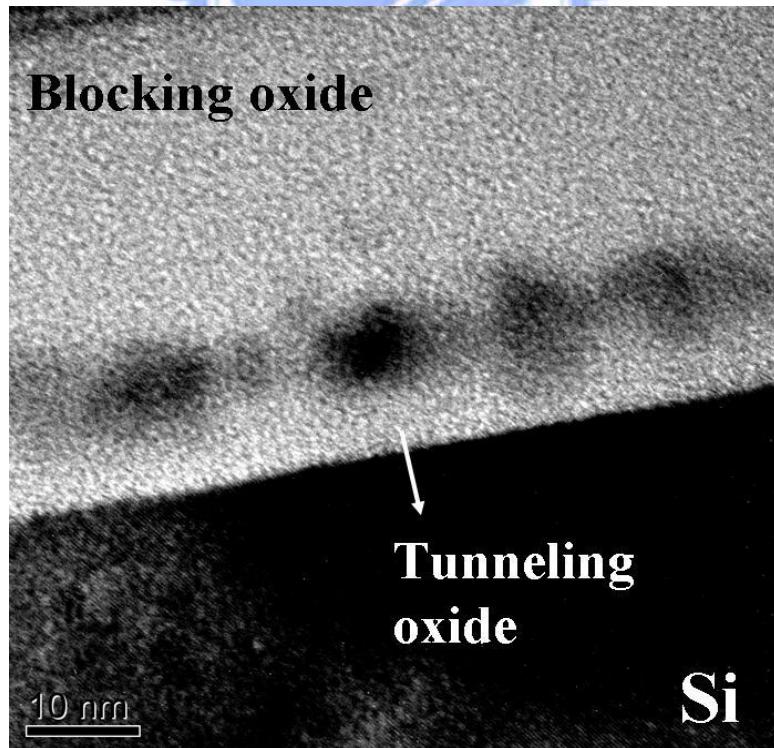


Figure 4-8 TEM diagram of the sample III ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) after RTA at 900°C for 60sec with PACO.

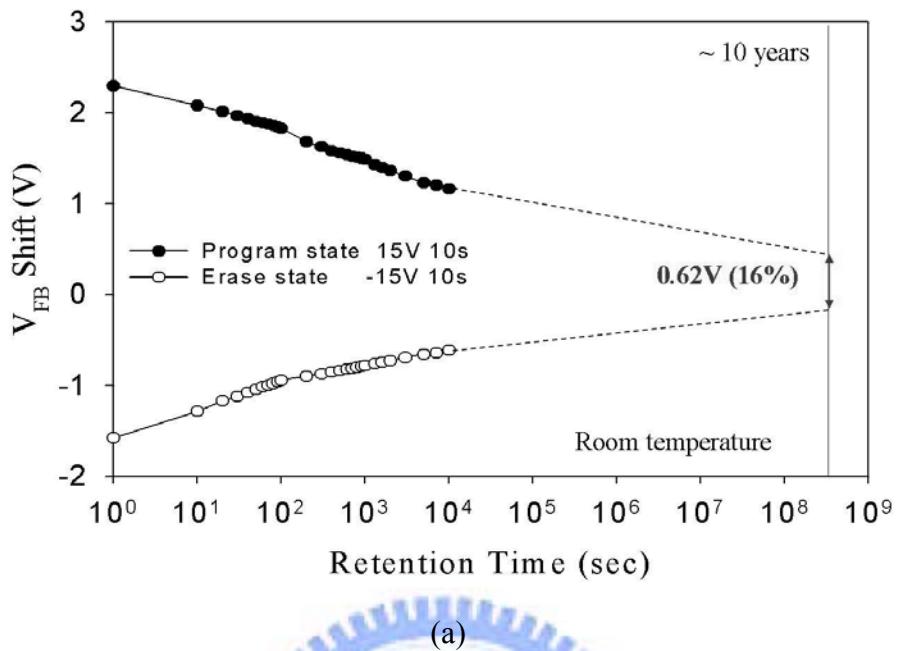


Figure 4-9 (a) Data retention characteristics of the Ge nanocrystals embedded in SiN_x memory with RTA at 900°C for 30sec.

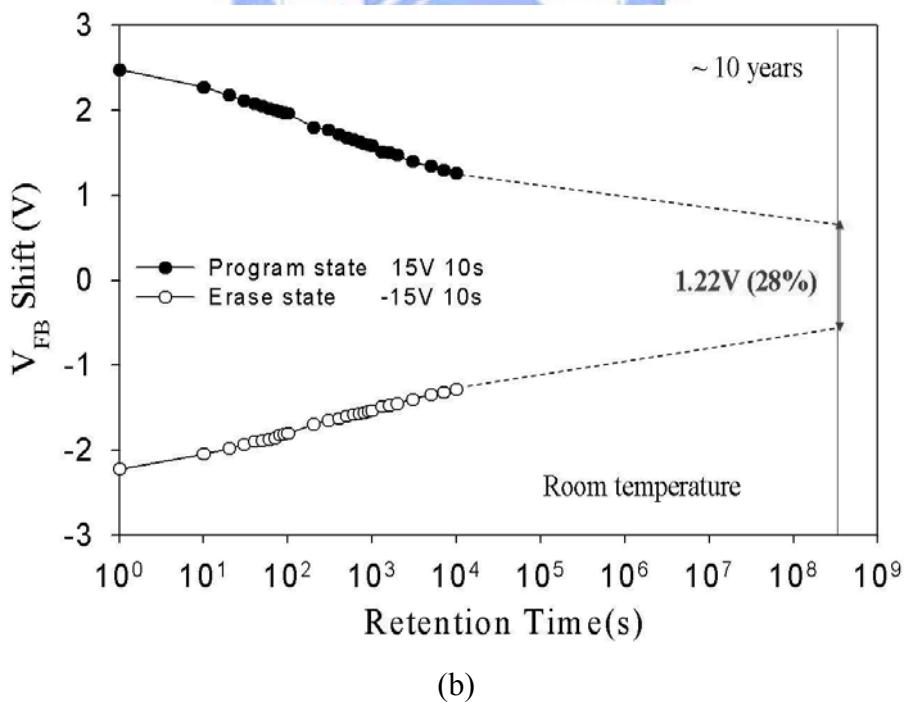
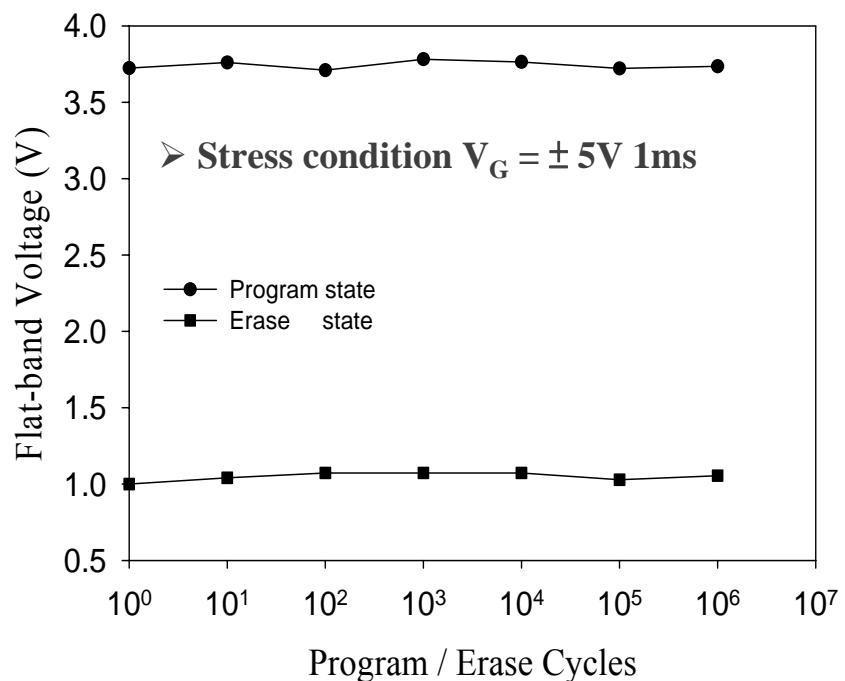
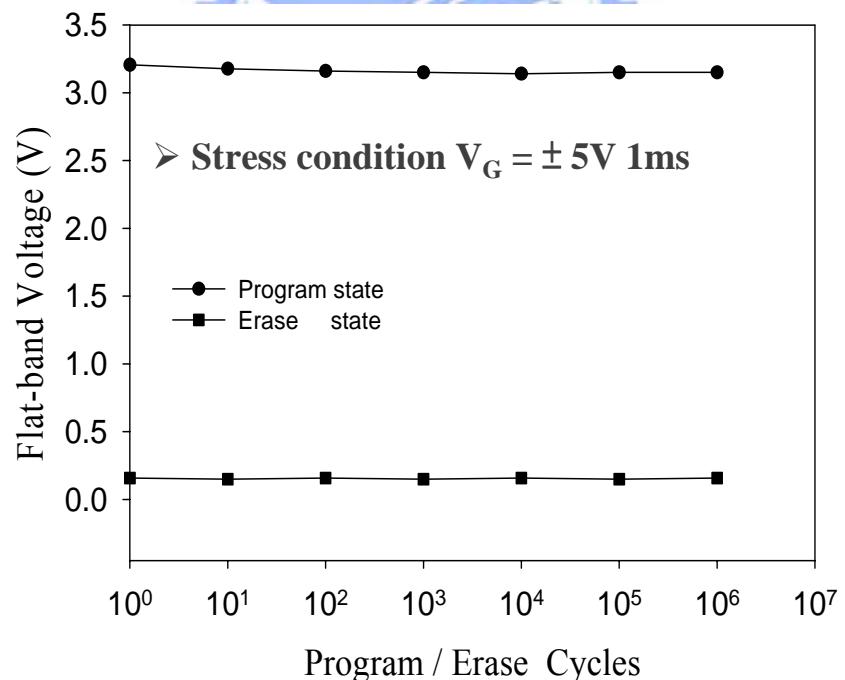


Figure 4-9 (b) Data retention characteristics of the Ge nanocrystals embedded in SiN_x memory with RTA at 900°C for 60sec.



(a)



(b)

Figure 4-10 Endurance characteristics of the Ge nanocrystal memory after RTA at (a) 900°C for 30sec (b) 900°C for 60sec.

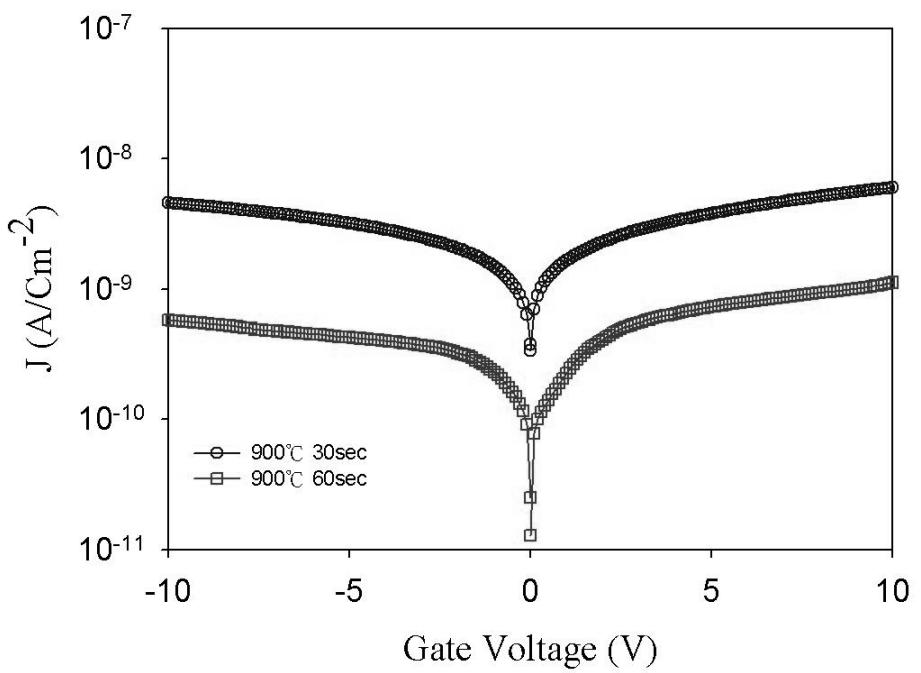


Figure 4-11 The current density-voltage (J-V) of Ge nanocrystals embedded in SiN_x memory with different thermal treatment (RTA) time.

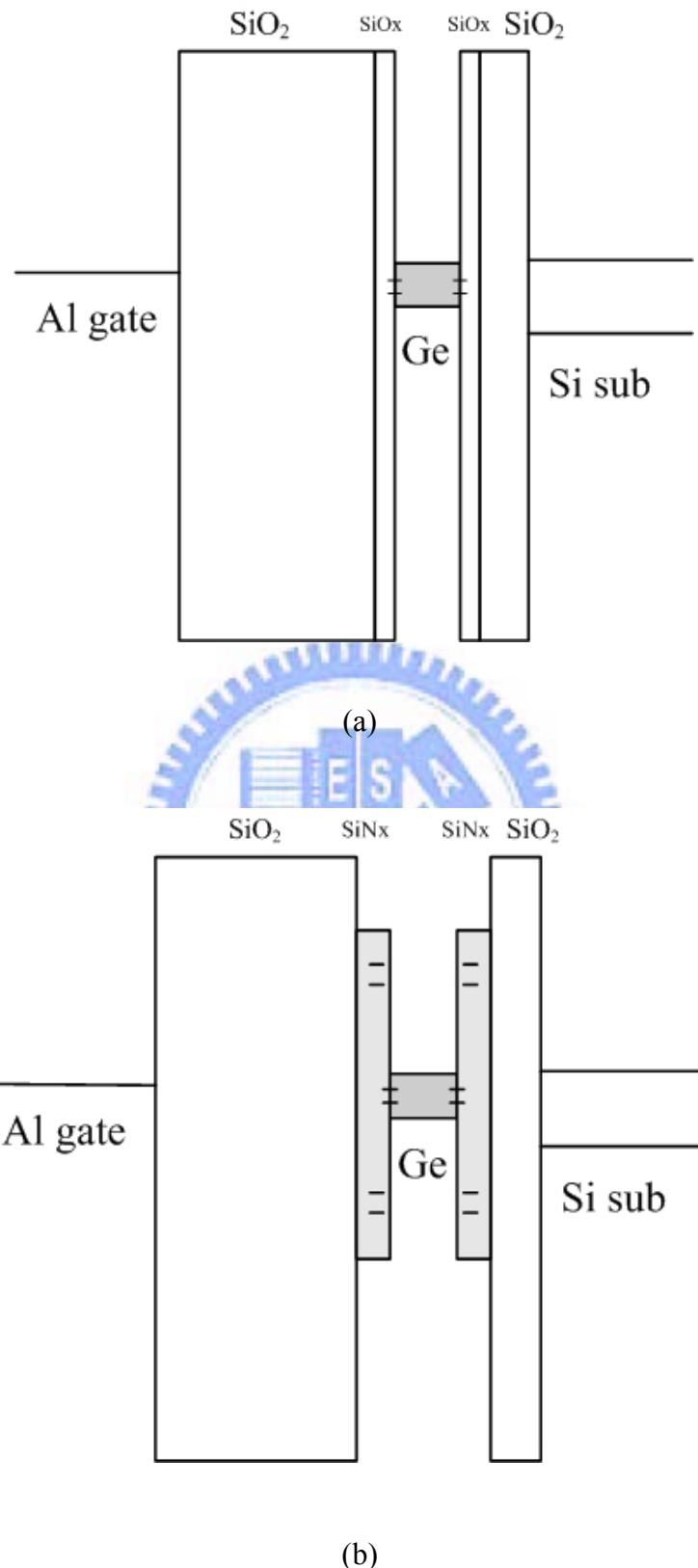


Figure 4-12 (a) and (b) The band diagram for Ge nanocrystals embedded in different dielectric memory. (a) in SiO_x (b) in SiN_x .

Chapter 5

Germanium doped Erbium Silicate high-*k* dielectric memory

5.1 Introduction

SONOS structure is still the mainstream for nonvolatile memory nowadays. More and more study was focused on the SONOS memory. In order to enhance the performance of SONOS memory, the new material was proposed, such as tunnel dielectric and charge trapping layer. The candidate material for tunnel dielectric is low barrier height, and the charge trap layer is trap-rich or higher band offset to the tunnel dielectric.

In recent research, high-*k* dielectric materials were proposed to replace the silicon nitride film as trapping layer, such as HfAlO and Al₂O₃ [5.1]. The over-erase phenomenon in the SONOS memory structure is minimized by using hafnium oxide (SOHOS) to replace silicon nitride (SONOS) as the charge storage layer. Unlike SONOS devices, SOHOS structures show a reduced over-erase phenomenon and self-limiting charge storage behavior under both erase and program operation. These are attributed to the differences in band offset and the crystallinity of the charge storage layer [5.2]. It was found that for a given electric field applied to the tunnel oxide, the programming speed of memory devices using HfO₂ film as a trapping layer is faster than that using Si₃N₄. According to the advantages of high-*k* dielectric, there are many researches with Ge nanocrystal embedded in high-*k* dielectric memory [5.3-5.5].

Various metal oxide have recently been suggested as high-*k*, which may serve as gate dielectrics when the thickness of SiO₂ will be reduced to where unacceptable leakage currents become unavoidable. One attractive class of high-*k* dielectrics are the rare-earth-metal oxides which offer high conduction band offsets, a large band gap and are also thermodynamically stable when deposited in a silicon substrate. Two rare-earth oxides have been reported as gate dielectrics recently, Y₂O₃ (*k*=12~18) and Gd₂O₃ (*k*=12~14) [5.6][5.7]. Erbium oxide is one of the rare-earth oxides, which have a numerous optical and electric characteristics. They, for example, can be used as

alternatives to silicon dioxide in gate dielectric related application. They offer a combination of high resistivity, high relative permittivity, large band gap and high chemical and thermal stability [5.8]. And erbium oxide is high-k dielectric, its dielectric constant is about 13 [5.9]. And some research is using high-k material silicate ex: Hf silicate, Zr silicate, for charging trap center memory [5.10]. Base on above researches, we doped Ge into erbium-rich high-*k* layer and observed its memory characteristics, in this chapter.

5.2 Experimental Sample Preparation

Figure 5-1 indicates a schematic of experimental procedure. This nonvolatile memory-cell structure in this study was fabricated on a 4 inches p-type silicon (100) wafer, which had been removed native oxide and particles by RCA process. After a standard RCA clean, a 5-nm-thick tunnel oxide was thermally grown by a dry oxidation process at 950°C in an atmospheric pressure chemical vapor deposition (APCVD) furnace. Subsequently, a 16-nm-thick oxygen and erbium incorporated $\text{Si}_{0.5}\text{Ge}_{0.5}$ (ErSiGeO) layer was deposited on tunnel oxide by co-sputtering of $\text{Si}_{0.5}\text{Ge}_{0.5}$ (80W) commixed target and Er (40W) target in the Ar/O_2 (24sccm/2sccm) ambience at room temperature. This step can obtain a quaternary layer as a charge trapping layer in our memory. We choose the $\text{Si}_{0.5}\text{Ge}_{0.5}$ target for this experiment due to previously result. $\text{Si}_{0.5}\text{Ge}_{0.5}$ target can allow enough Ge concentration in the deposited film.

In order to prevent the Ge interacting with the oxygen in the chamber resulting GeO out-diffusion during rapid thermal anneal (RTA) process. We deposited a 5-nm-thick PECVD oxide on the trapping layer before RTA. We called this step “pre-annealing-capping-oxide” (PACO). After that, we annealed the sample by RTA at 900°C for 30sec in N_2 ambience. After RTA process, a 35-nm-thick blocking oxide was deposited by PECVD at 300°C. Al gate electrodes on back and front side of the sample were finally deposited and patterned to form a metal/oxide/insulator/oxide/silicon (MOIOS) structure. And we noted this MOIOS structure for “**Sample IV**”.

The capacitance-voltage (C-V) hysteresis characteristic was also performed by Keithley 4200 and HP4284 Precision LCR Meter with high frequency 1 MHz. In addition, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) were adopted for the micro-structure analysis and chemical material analysis.

5.3 Results and discussion

Figure 5-2 shows typical cross-section TEM image of the control sample. We can observe that 16-nm dielectric was deposited uniformly on the tunnel oxide. And we made Energy Dispersive X-ray Spectrometer (EDS) analysis. The result of EDS is shown in table 5-1. Notice that we did not detect the silicon and oxygen atoms. Because that we might get some part of Si and O signal contributed by blocking oxide and tunnel oxide. From the table 5-1, we can know that the trapping layer we deposited is an erbium-rich (Er : Ge = 3 : 1) similar to high- k layer. Figure 5-3 shows the capacitance-voltage (C-V) hysteresis of control sample (without any thermal treatment). It is obviously that the control samples show no memory effect.

Figure 5-4 shows cross-section TEM diagram of the sample with PACO after RTA at 900°C for 30sec. Figure 5-4 looks like similar to the figure 5-2. In the TEM pictures, the image does not change a lot after thermal treatment. But the XPS analysis shown in figure 5-5 shows some difference. The Er 4d core-level spectrum is shown in figure 5-5 before and after RTA at 900°C for 30sec. According to literature, the bonding energy of Er-O bond is about 168.7 eV. And after RTA, the Er 4d core-level spectrum peak shift toward higher binding. Some high- k materials such as hafnium (Hf) and zirconium (Zr) their oxide, like HfO_2 ZrO_2 , when the metal-O bonds react with their nearby Si atoms, the signal peak will shift to higher bonding energy position [5.10][5.11]. Therefore, we think the Er-O might get bonding with Si and became erbium silicate high- k dielectric.

Figure 5-6 shows the forward and reverse sweep C-V characteristics, indicating the electron charging and discharging effects of Ge doped erbium silicate high- k dielectric memory. It is obviously observed that 5.3V and 13V memory windows can be obtained under $\pm 5\text{V}$ and $\pm 10\text{V}$ operation, respectively. The C-V hysteresis loops are counterclockwise, which is due to injection of electron from the deep inversion layer and injection of holes from the accumulation layer of silicon substrate. The larger memory window is due to the high- k material supply some additional traps and has better program/erase speed.

5.4 Summary III

In this chapter, a SONOS type memory with erbium silicate high- k dielectric was obtained by sputtering deposition followed by a less thermal budget (RTA at 900°C for 30sec) process. We demonstrated the high- k dielectric has charging storage ability and faster program/erase speed. In addition, significant C-V shift of 13V with operating at $\pm 10\text{V}$ sweeping voltage, which is larger than above Ge nanocrystals embedded in SiO_x or

SiN_x memory as shown in table 5-2.



Element	Weight%	Atomic%
Ge K	13.81	26.97
Er L	86.19	73.03
Totals	100.00	100.00

Table 5-1 Energy Dispersive X-ray Spectrometer (EDS) analysis of the control sample IV (ErSiGeO).

Memory window under $\pm 10V$	Ge NCs embedded in SiO_x (Ge - poor)	Ge NCs embedded in SiO_x (Ge - rich)	Ge NCs embedded in SiN_x	Ge doped ErSiO dielectric
STD	×	×	×	×
RTA 900°C 30s	0.65V	2.8V	3.2V	13V
RTA 900°C 60s		3.1V	3.75V	

Table 5-2 Comparison of memory window under $\pm 10V$ sweeping operation with different samples and thermal treatment conditions (with PACO).

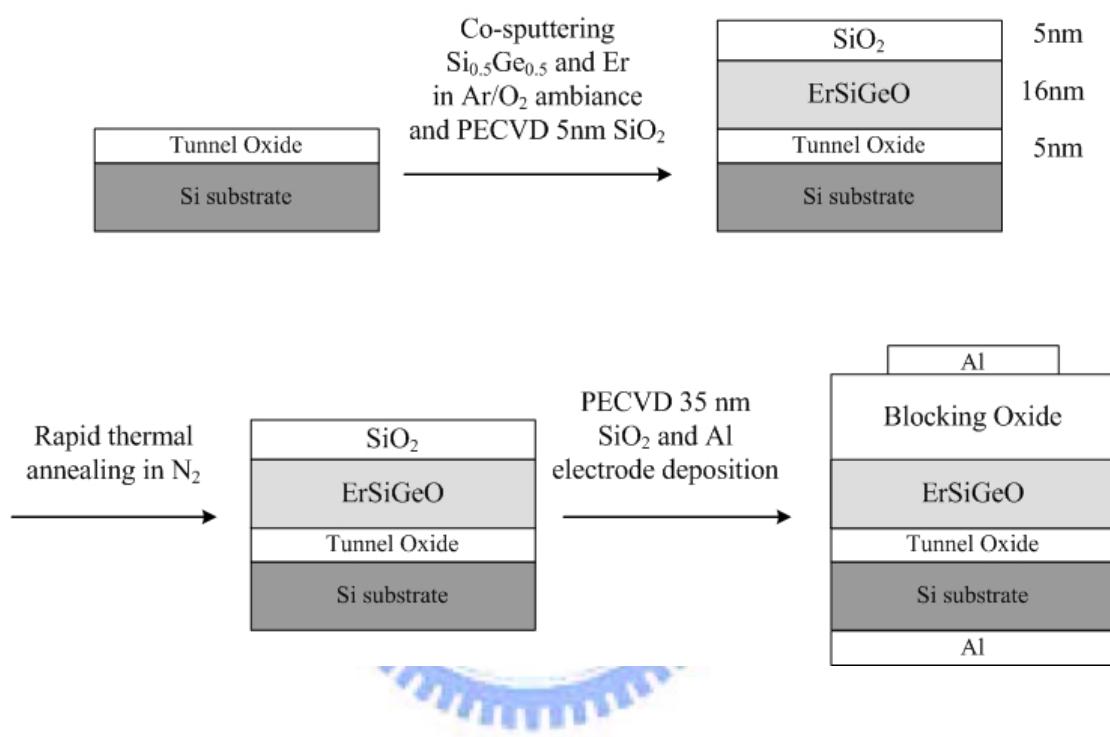


Figure 5-1 The process flow for co-sputtering Si_{0.5}Ge_{0.5} commixed target and Er target in Ar/O₂ ambience with pre-annealing capping oxide (PACO) step.

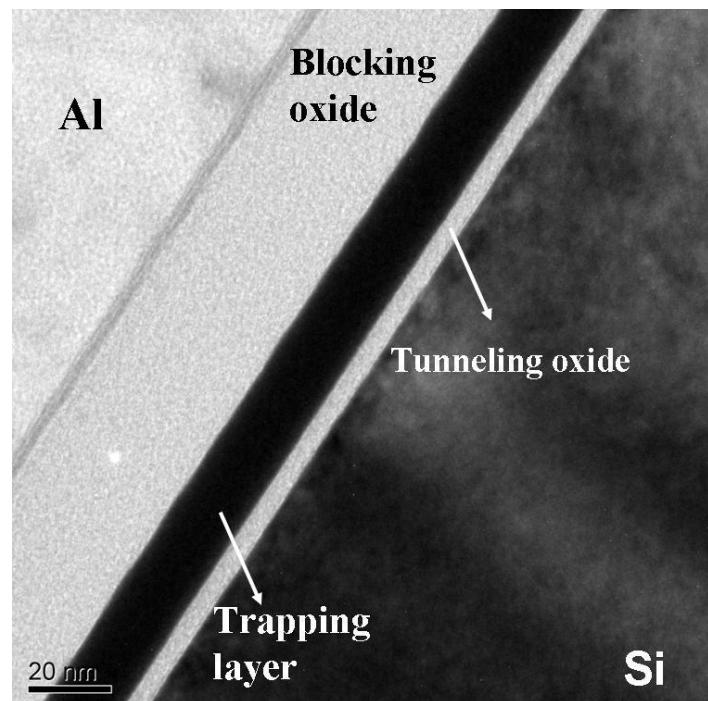


Figure 5-2 Cross-sectional TEM images of standard Sample IV ($\text{ErSi}_{0.5}\text{Ge}_{0.5}\text{O}$) without any thermal treatment.

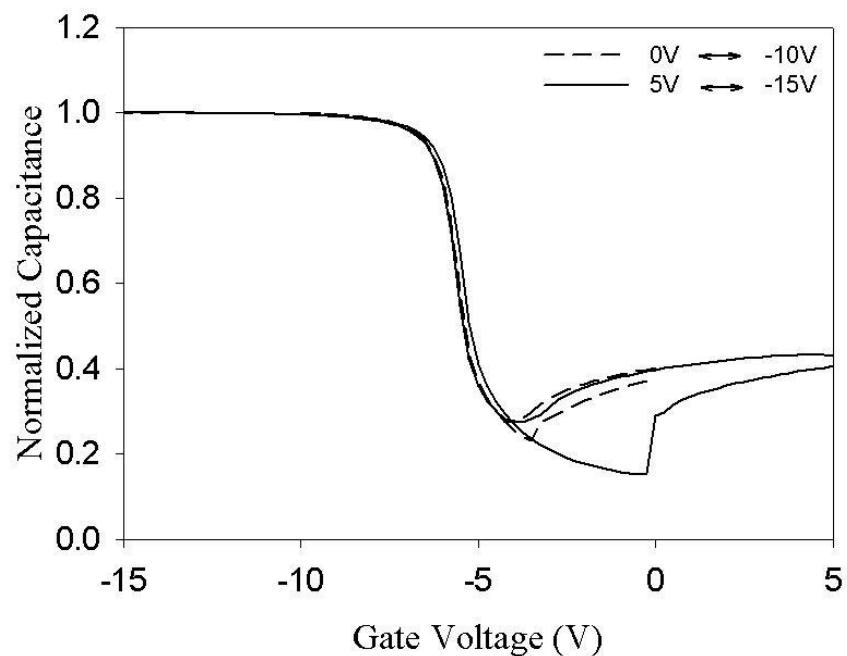


Figure 5-3 Capacitance-voltage (C-V) hysteresis of standard sample IV ($\text{ErSi}_{0.5}\text{Ge}_{0.5}\text{N}$) without any thermal treatment.

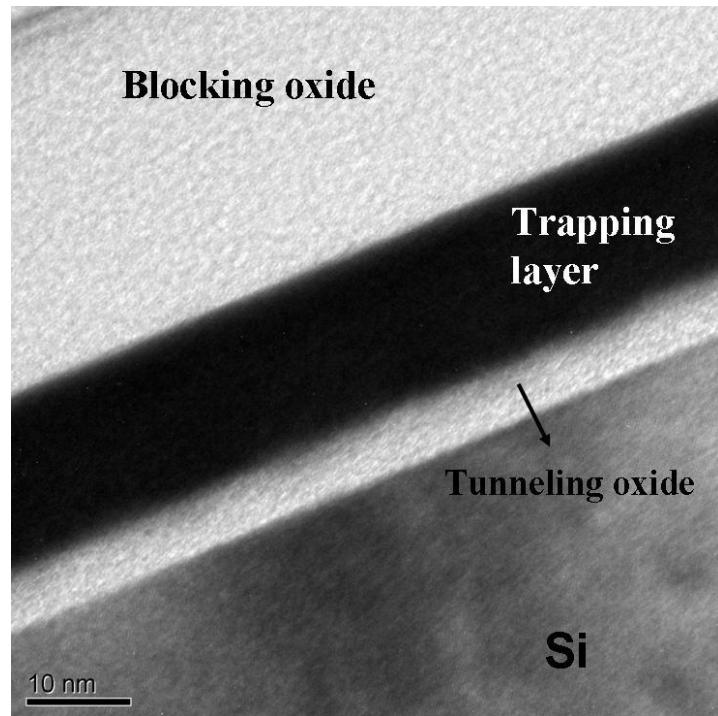


Figure 5-4 Cross-sectional TEM diagram of the sample IV ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{N}$) after RTA at 900°C for 30sec with PACO.

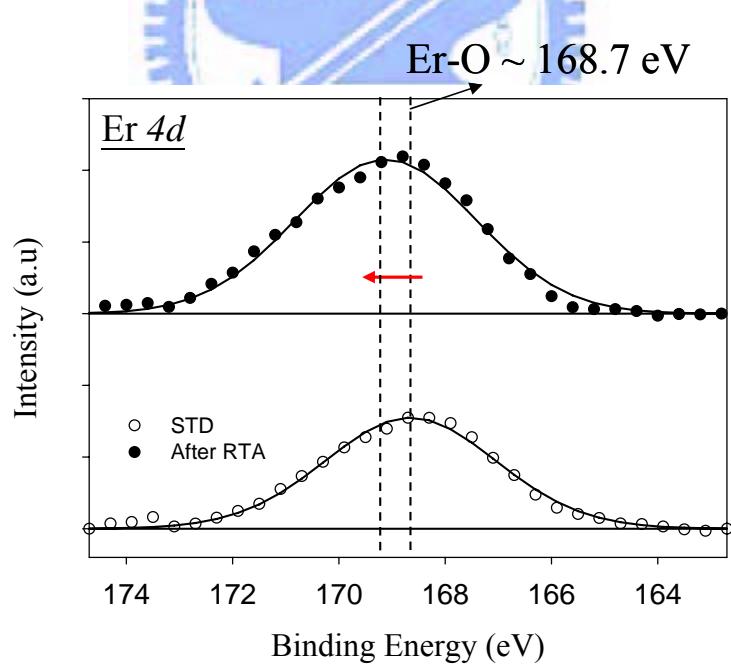


Figure 5-5 The XPS analysis of Er 4d core-level spectrum for sample IV before and after RTA. After the RTA process, the peak signal of Er-O bonding shift toward higher binding energy indicating Er-O might react with their nearby Si atoms.

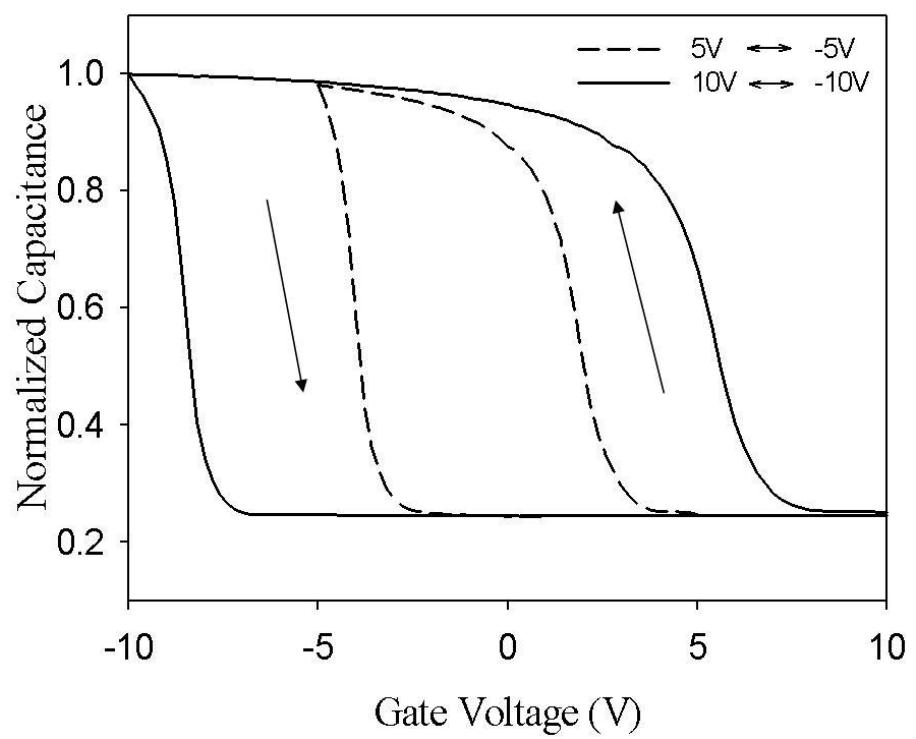


Figure 5-6 Capacitance-voltage (C-V) hysteresis of sample IV after RTA at 900°C for 30sec with PACO.

Chapter 6

Conclusions

6.1 Conclusions

In this study, a novel and simple fabrication of Ge nanocrystal was proposed and demonstrated for the application of nonvolatile semiconductor memory. The nonvolatile memory with Ge nanocrystals embedded in silicon oxide (SiO_x) layer was fabricated by reactive sputtering a commixed target ($\text{Si}_x\text{Ge}_{1-x}$) in Ar/O_2 ambiance. We successfully incorporated oxygen into SiGe layer to form SiGeO ternary layer. After that we do not need to consider about Ge over-oxidation phenomena and add extra high pressure hydrogen annealing to return Ge oxide to Ge. And we find out that pre-annealing-capping-oxide (PACO) to avoid GeO out-gassing is a critical step in our experiments.

During a rapid thermal annealing (RTA) at 900°C for 30seconds process, the Ge atoms will segregate and nucleate to form Ge nanocrystals (or Ge nano-dots). The high area density ($\sim 10^{12}\text{cm}^{-2}$) nanocrystal can be fabricated simply. We can improve the performance just by annealing 30 more seconds at 900°C which makes better isolation of Ge nanocrystals and reduces the defects (lateral leakage path) in the dielectric (SiO_x) surrounding Ge nanocrystals. According the better isolation of Ge nanocrystals, longer thermal treatments cause larger memory window. And the reliability issue, especially retention is significantly improved.

Another similar process for Ge nanocrystals embedded in silicon nitride (SiN_x) was also proposed by reactive sputtering a commixed SiGe target ($\text{Si}_{0.5}\text{Ge}_{0.5}$) in Ar/N_2 ambiance. We incorporated nitrogen into SiGe layer to form SiGeN ternary layer. After a rapid thermal annealing (RTA), the Ge atoms will precipitate to form Ge nanocrystals embedded in SiN_x . The charge storage layer of nanocrystals embedded in SiN_x exhibits larger memory characteristics over nanocrystals embedded in SiO_x . The improvement of charge storage capacity is attributed to additional accessible charge trap states in the SiN_x matrix.

As the same, increasing the thermal treatment time can improve the isolation of Ge nanocrystals and reduce the defects above the nanocrystal in the SiN_x dielectric. That is

the reason for 900°C 60 seconds sample showing not only larger memory window but also better retention than 30 seconds one. And all of above nanocrystal memories exhibit excellent endurance characteristics indicating the quality of tunnel oxide grown by APCVD at 950°C is strengthened enough to bear 10^6 P/E cycles stress. Finally, the fabrication technique for the application of the above nonvolatile nanocrystal memory can be compatible with current process of the integrated circuit manufacture.

A SONOS type memory with erbium silicate high- k dielectric was obtained by sputtering deposition followed by a thermal budget (RTA at 900°C for 30 seconds) process. We demonstrated the high- k dielectric has charging storage ability and faster program/erase speed. In addition, significant C-V shift of 13V with operating at ± 10 V sweeping voltage, which is larger than above Ge nanocrystals embedded in SiO_x or SiN_x memory. And it is suitable for the application of low-power nanoscaled nonvolatile memory.



References

Chapter 1:

- [1.1] P. Pavan, R. Bez, P. Olivo, and E. Zanoni, “Flash memory cells—An overview” *Proc. IEEE*, vol. 85, pp. 1248–1271, Aug. 1997.
- [1.2] Roberto Bez, Emilio Camerlenghi, Alberto Modelli, and Angelo Visconti, “Introduction to Flash Memory” *Proc. IEEE*, vol. 91, No.4, April 2003.
- [1.3] D. Kahng and S. M. Sze, “A floating gate and its application to memory devices”, *Bell Syst. Tech*, 46, 1288 1967.
- [1.4] J. D. Blauwe, “Nanocrystal nonvolatile memory devices”, *IEEE Transaction on Nanotechnology*, Vol. 1, pp. 72-77, 2002.
- [1.5] M. H. White, Y. Yang, A. Purwar, and M. L. French, ”A low voltage SONOS nonvolatile semiconductor memory technology”, *IEEE Int'l Nonvolatile Memory Technology Conference*, 52 1996.
- [1.6] M. H. White, D. A. Adams, and J. Bu, “On the go with SONOS,” *IEEE circuits & devices*, 16, 22 2000.
- [1.7] H. E. Maes, J. Witters, and G. Groeseneken, *Proc. 17 European Solid State Devices Res. Conf. Bologna 1987*, 157 1988.
- [1.8] S. Tiwari, F. Rana, K. Chan, H. Hanafi, C. Wei, and D. Buchanan, “Volatile and non-volatile memories in silicon with nano-crystal storage”, *IEEE Int. Electron Devices Meeting Tech. Dig.*, 521-524, 1995.
- [1.9] J. J. Welser, S. Tiwari, S. Rishton, K. Y. Lee, and Y. Lee, “Room temperature operation of a quantum-dot flash memory”, *IEEE Electron Device Lett.*, 18, 278 1997.
- [1.10] Y. C. King, T. J. King, and C. Hu, “MOS memory using germanium nanocrystals formed by thermal oxidation of $Si_{1-x}Ge_x$ ”, *IEEE Int. Electron Devices Meeting Tech. Dig.*, 115 1998.
- [1.11] Y. Yang, A. Purwar and M. H. White, “Reliability considerations in scaled SONOS nonvolatile memory devices”. *Solid-State Electronics*, Vol. 43, pp.2025-2032, 1999.
- [1.12] H.A.R. Wegener, A.J. Lincoln, H.C. Pao, M.R. O'Connell, and R.E. Oleksiak, The variable threshold transistor, a new electrically alterable, non-destructive

read-only storage device," *IEEE IEDM Tech. Dig.*, Washington, D.C., 1967.

[1.13] T.Y.Chan, K.K.Young and C.Hu, "A true single-transistor oxide- nitride-oxide EEPROM device". *IEEE Electron Device Letters*, vol.8, no.3, pp.93-95, 1987.

[1.14] M.K. Cho and D.M.Kim, "High performance SONOS memory cells free of drain turn-on and over-erase: compatibility issue with current flash technology", *IEEE Electron Device Letters*, pp.399-401, Vol.21, No.8, 2000.

[1.15] I. Fijiwara, H.Aozasa, K.Nomoto, S.Tanaka and T.Kobayashi, " High speed program/erase sub 100nm MONOS memory cell", *Proc. 18th Non-Volatile Semiconductor Memory Workshop*, p. 75, 2001.

[1.16] C. Tung-Sheng, W. Kuo-Hong, C. Hsien, and K. Chi-Hsing, "Performance improvement of SONOS memory by bandgap engineering of charge-trappinglayer", *IEEE Electron Device Lett.*, vol. 25, no. 3, pp.205–207, Mar. 2004.

[1.17] Min She, Hideki Takeuchi, and Tsu-Jae King, "Silicon-Nitride as a Tunnel Dielectric for Improved SONOS-Type Flash Memory", *IEEE Electron Device Letters*, vol. 24, no. 5, MAY 2003.

[1.18] Shih-Ching Chen, Ting-Chang Chang, Po-Tsun Liu, Yung-Chun Wu, and Ping-Hung Yeh, "Nonvolatile polycrystalline silicon thin-film-transistor memory with oxide/nitride/oxide stack gate dielectrics and nanowire channels", *Applied Physics Letters*, vol. 90, 122111, 2007.

[1.19] T. Sugizaki, M. Kobayashi, M. Ishidao, H. Minakata, M. Yamaguchi, Y. Tamura, Y. Sueivama, T. Nakanishi and H. Tanaka, "Novel Multi-bit SONOS Type Flash Memory Using a High-k Charge Trapping Layer", *Dig Tech Pap Symp VLSI Technol.*, p.27, 2003.

[1.20] Y. N. Tan, W. K. Chim, W. K. Choi, M. S. Joo, T. H. Ng and B. J. Cho, "A MONOS-Type Flash Memory Using a High-k HfAlO Charge Trapping Layer", *Electrochem. Solid-State Lett.*, Volume 7, Issue 9, pp. G198-G200, 2004.

[1.21] Y. N Tan, W. K Chim, B. J. Cho and W. K. Choi, "Over-erase phenomenon in SONOS-type flash memory and its minimization using a hafnium oxide charge storage Layer", *IEEE Trans. Elec. Dev.*, vol. 51, pp. 1143-1147, 2004.

[1.22] J. J. Welser, S. Tiwari, S, Rishton, K.Y. Lee and Y. Lee, "Room temperature operation of a quantum-dot flash memory", *IEEE Electron Device Letter*, vol.18, pp. 278-280, 1997.

[1.23] J De Blauwe, "Nanocrystal nonvolatile memory devices", *IEEE Trans.*

Nanotechnology, vol. 1, issue 1, 2002.

- [1.24] R. Ohba, N. Sugiyama, K. Uchida, J. Koga, and A. Toriumi, “Nonvolatile Si quantum memory with self-align doubly-stacked dots”, *IEEE Trans. Electron Devices*, Vol. 49, issue 8, pp. 1392-1398. 2002.
- [1.25] Y. C. King, T. J. King, and C. Hu, “Charge-trap memory device fabricated by oxidation of $\text{Si}_{1-x}\text{Ge}_x$ ”, *IEEE Trans. Electron Devices*, Vol. 48, pp. 696-700, 2001.
- [1.26] M. She, Y. C. King, T. J. King, C. Hu, “Modeling and design study of nanocrystal memory devices”, *IEEE Device Research Conference*, pp. 139-140. 2001.
- [1.27] I. Kim, S. Han, K. Han, J. Lee, H. Shin, ”Room temperature single electron effects in a Si nano-crystal memory,” *IEEE Electron Device Lett.*, vol.20, pp. 630-631, 1999.
- [1.28] I. Kim, S. Han, H. Kim, J. Lee, B. Choi, S. Hwang, D. Ahn, H. Shin, “Room temperature single electron effects in Si quantum dot memory with oxide-nitride tunneling dielectrics”, *Technical Digest - International Electron Devices Meeting*, pp.111-114, 1998.
- [1.29] A. Fernandes, B. DeSalov, T. Baron *et al*, “Memory characteristics of Si quantum dot devices with $\text{SiO}_2/\text{ALD Al}_2\text{O}_3$ tunneling dielectrics”, *Technical Digest - International Electron Devices Meeting*, pp.155-158, 2001.
- [1.30] F. K. LeGoues, R. Rosenberg, T. Nguyen, F. Himpel, B. S. Meyerson, “Oxidation of SiGe,” *J. Appl. Phys.*, Vol. 65, pp.1724-1728, 1989.
- [1.31] J. Eugene, F. K. LeGoues, V. P. Kesan. S. S. Iyer, F. M. d’Heurle. “Diffusion versus oxidation rates in silicon-germanium alloys”, *Applied Physics Letters*, vol. 59, pp. 78-80, 1991.
- [1.32] M. L. Ostraat, J. W. DeBlauwe, M. L. Green, L. D. Bell, M.L. Brongersma, J. Casperson, R. C. Flagan, H. A. Atwater, “Synthesis and characterization of aerosol silicon nanocrystal nonvolatile floating-gate memory device”, *Applied Physics Letters*, vol. 79, pp. 433-435, 2001.
- [1.33] J. J. Lee, X. Wang, W. Bai, N. Lu, D. L. Kwong, “Theoretical and experimental investigation of Si nanocrystal memory device with HfO_2 high- k tunneling dielectric”. *IEEE Trans. Electron Devices*, Vol. 50, pp. 2067, 2002.
- [1.34] L. Guo, E. Leobandung, and S. Y. Chou, “Si single-electron MOS memory with nanoscale floating-gate and narrow channel,” *Technical Digest-International Electron Devices Meeting*, pp. 955-956, 1996.

- [1.35] N. Takahashi, H. Ishikuro, and T. Hiramoto, “A directional current switch using silicon electron transistors controlled by charge injection into silicon nano-crystal floating dots”, *Technical Digest-International Electron Devices Meeting*, pp. 371–374, 1999.
- [1.36] J. Wahl, H. Silva, A. Gokirmak, A. Kumar, J. J. Welser, and S. Tiwari, “Write, erase and storage times in nanocrystal memories and the role of interface states”, *Technical Digest-International Electron Devices Meeting*, pp. 375–378, 1999.

Chapter 2:

- [2.1] P. Pavan, R. Bez, P. Olivo, and E. Zanoni, “Flash memory cells - an overview”, *Proceedings of The IEEE*, Vol. 85, No. 8, pp. 1248-1271, 1997.
- [2.2] M. Woods, *Nonvolatile Semiconductor Memories: Technologies, Design, and Application*, C. Hu, Ed. New York: IEEE Press, Ch. 3, p. 59, 1991.
- [2.3] P. E. Cottrell, R. R. Troutman, and T. H. Ning, “Hot-electron emission in n-channel IGFETs”, *IEEE Journal of Solid-State Circuits*, Vol.14, pp. 442-455, 1979.
- [2.4] B. Eitan and D. Froham-Bentchkowsky, “Hot-electron injection into the oxide in n-channel MOS devices”, *IEEE Trans. Electron Devices*, Vol. 28, pp. 328-340, 1981.
- [2.5] Chenming. Hu, “Lucky-electron model of channel hot electron emission”, *Technical Digest-International Electron Devices Meeting*, pp. 22-25, 1979.
- [2.6] S. Tam, P. K. Ko, C. Hu, and R. Muller, “Correlation between substrate and gate currents in MOSFET's”, *IEEE Trans. Electron Devices*, Vol. 29, pp. 1740-1744, 1982.
- [2.7] T. Ohnakado, H. Onoda, O. Sakamoto, K. Hayashi, N. Nishioka, H. Takada, K. Sugahara, N. Ajika and S. Satoh, “Device characteristics of 0.35 μm P-channel DINOR flash memory using band-to-band tunneling-induced hot electron (BBHE) programming”, *IEEE Trans. Electron Devices*, Vol. 46, pp. 1866-1871, 1999.
- [2.8] J. Bu, M. H. White, ”Design considerations in scaled SONOS nonvolatile memory devices”, *Solid-State Electronics.*, Vol. 45, pp. 113-120, 2001.
- [2.9] M. L. French, M. H. White., “Scaling of multiedielectric nonvolatile SONOS memory structures”, *Solid-State Electronics.*, Vol. 37, pp. 1913-1923, 1994.
- [2.10] M. L. French, C. Y. Chen, H. Sathianathan, M. H. White., “Design and scaling of a SONOS multiedielectric device for nonvolatile memory applications”, *IEEE Transactions on Components, Packaging, and Manufacturing Technology Part A*,

Vol. 17, pp. 390-397, 1994.

- [2.11] Y. S. Hisamune, K. Kanamori, T. Kubota, Y. Suzuki, M. Tsukiji, E. Hasegawa, A. Ishitani, and T. Okazawa, "A high capacitive-coupling ratio (HiCR) cell for 3 V-only 64 Mbit and future flash memories", *Technical Digest-International Electron Devices Meeting*, pp. 19-22, 1993.
- [2.12] Z. Liu, C. Lee, V. Narayanan, G. Pei, and E. C. Kan, "Metal nanocrystal memories. I. Device design and fabrication", *IEEE Trans. Electron Devices*, Vol. 49, pp. 1606-1613, 2002.
- [2.13] J. Moll, *Physics of Semiconductors*. New York: McGraw-Hill, 1964.
- [2.14] M. Lezlinger and E. H. Snow, "Fowler-Nordheim Tunneling into Thermally Grown SiO₂", *Journal of Applied Physics*, Vol.40, pp. 278-283, 1969.
- [2.15] Christer Sevensson and Ingemar Lundstrom, "Trap-assisted charge injection in MNOS structures", *Journal of Applied Physics*, Vol.44, pp. 4657-4663, 1973.
- [2.16] I. C. Chen, C. Kaya, J. Paterson, "Band-to-band tunneling induced substrate hot-electron (BBISHE) injection: a new programming mechanism for nonvolatile memory devices", *Technical Digest-International Electron Devices Meeting*, pp.263-266, 1989.
- [2.17] I. C Chen, D. J. Coleman, and C. W. Teng, "Gate current injection initiated by electron band-to-band tunneling in MOS devices", *IEEE Electron Device Lett.*, vol.10, pp. 297-300, 1989.
- [2.18] T. Ohnakado, K. Mitsunaga, M. Nunoshita, H. Onoda, K. Sakakibara, N. Tsuji, N. Ajika, M. Hatanaka and H. Miyoshi, "Novel electron injection method using band-to-band tunneling induced hot electrons (BBHE) for flash memory with a P-channel cell", *Technical Digest-International Electron Devices Meeting*, pp. 279-282, 1995.
- [2.19] Suk-Kang Sung, Il-Han Park, Chang Ju Lee, Yong Kyu Lee, Jong Duk Lee, Byung-Gook Park, Soo Doo Chae, and Chung Woo Kim, "Fabrication and Program/Erase Characteristics of 30-nm SONOS Nonvolatile Memory Devices," *IEEE Transactions on Nanotechnology*, Vol.2, No.4, pp. 258-264, 2003.
- [2.20] R. Bez, E. Camerlenghi, A. Modelli, and A. Visconti, "Introduction to flash memory", *Proceedings of The IEEE*, Vol. 91, pp. 489-502, 2003.
- [2.21] P. Cappelletti, R. Bez, D. Cantarelli, and L. Fratin, "Failure mechanisms of flash cell in program/erase cycling", *Technical Digest-International Electron Devices Meeting*, pp. 291-294, 1994.

- [2.22] D. Ielmini, A. Spinelli, A. Lacaita, and A. Modelli, “Statistical model of reliability and scaling projections for Flash memories”, *Technical Digest-International Electron Devices Meeting*, pp.32.2.1–32.2.4, 2001.
- [2.23] D. Ielmini, A. S. Spinelli, A. L. Lacaita, L. Confalonieri, and A. Visconti, “New technique for fast characterization of SILC distribution in Flash arrays”, *Annual Proceedings - Reliability Physics (Symposium)*, pp. 73–80, 2001.
- [2.24] D. Ielmini, A. S. Spinelli, A. L. Lacaita, R. Leone, and A. Visconti, “Localization of SILC in Flash memories after program/erase cycling”, *Annual Proceedings - Reliability Physics (Symposium)*, pp. 1–6, 2002.
- [2.25] Y. M. Niquet, G. Allan, C. Delerue, M. Lannoo, “Quantum confinement in germanium nanocrystals,” *Applied Physics Letters*, vol.77, pp.1182-1184 2000.
- [2.26] T. Takagahara , K.Takeda, “Theory of the quantum confinement effect on excitons in quantum dots of indirect- gap materials,” *Phys. Rev. B*, Vol. 46, pp. 15578-15581, 1992.
- [2.27] J.D.Jackson, “Classcial Electrodynamics”, published by John Wiley & Sons, 1999.

Chapter 3:

- [3.1] Roberto Bez, Emilio Camerlenghi, Alberto Modelli, and Angelo Visconti, “Introduction to Flash Memory” *Proc. IEEE*, vol. 91, No.4, April 2003.
- [3.2] J. D. Blauwe, “Nanocrystal nonvolatile memory devices”, *IEEE Transaction on Nanotechnology*, Vol. 1, pp. 72-77, 2002.
- [3.3] C. Y. Lu, T. C. Lu, and R. Liu, “Non-volatile memory technology - Today and tomorrow”, *Proceedings of 13th International Symposium on the Physical and Failure Analysis of Integrated Circuits, IPFA.*, pp. 18-23, 2006.
- [3.4] S. Tiwari, F. Rana, K. Chan, H. Hanafi, C. Wei, and D. Buchanan, “Volatile and non-volatile memories in silicon with nano-crystal storage”, *IEEE Int. Electron Devices Meeting Tech. Dig.*, 521-524, 1995.
- [3.5] J. H. Jung, J. Y. Jin, I. Lee, T. W. Kim, H. G. Roh, Y. H. Kim, ”Memory effect of ZnO nanocrystals embedded in an insulating polyimide layer”, *Applied Physics Letters*, vol. 88, 112107, 2006.
- [3.6] Y. C. King, T. J. King, C. Hu, “Charge-trap memory device fabricated by oxidation of $Si_{1-x}Ge_x$ ”, *IEEE Trans. Electron Devices*, Vol. 48, pp. 696-700, 2001.
- [3.7] HI. Hanafi, S. Tiwari, I. Khan, “Fast and long retention-time nano-crystal memory,” *IEEE Trans. Electron Devices*, Vol. 43, No.9, pp. 1553-1558, 1996.

[3.8] S. Duguay, J. J. Grob, A. Slaoui, Y. Le Gall, and M. Amann-Liess, “Structural and electrical properties of Ge nanocrystals embedded in SiO_2 by ion implantation and annealing”, *J. Appl. Phys.*, Vol.97, pp.104330, 2005.

[3.9] T. Sass, V. Zela, A. Gustafsson, I. Pietzonka, W. Seifert, “Continuous formation and faceting of SiGe islands on Si(100)”, *Applied Physics Letters*, Vol. 81, pp. 3454-3456, 2002.

[3.10] V. Craciun, I. W. Boyd, A. H. Reader, W. J. Kersten, F. J. G. Hakkens, P. H. Oosting, D. E. W. Vandenhoudt, ” Microstructure of oxidized layers formed by the low-temperature ultraviolet-assisted dry oxidation of strained $\text{Si}_{0.8}\text{Ge}_{0.2}$ layers on Si “, *J. Appl. Phys.*, Vol.75, pp.1972-1976, 1994.

[3.11] A. Kanjilal, J. Lundsgaard Hansen, P. Gaiduk, A. Nylandsted Larsen, N. Cherkashin, A. Claverie, P. Normand, E. Kapelanakis, D. Skarlatos, D. Tsoukalas, ” Structural and electrical properties of silicon dioxide layers with embedded germanium nanocrystals grown by molecular beam epitaxy”, *Applied Physics Letters*, Vol. 82, pp. 1212-1214, 2003.

[3.12] H. Fukuda, T. Kobayashi, T. Endoh, S. Nomura, A. Sakai, Y. Ueda, “Growth and characterization of Ge nanocrystals in ultrathin SiO_2 films”, *Applied Surface Science*, 130, pp. 776-780, 1998.

[3.13] W. K. Choi, W. K. Chim, C. L. Heng, L. W. Teo, Vincent Ho, V. Ng, D. A. Antoniadis, E. A. Fitzgerald,” Observation of memory effect in germanium nanocrystals embedded in an amorphous silicon oxide matrix of a metal–insulator–semiconductor structure”, *Applied Physics Letters*, Vol. 80, pp. 2014-2016, 2002.

[3.14] W. S. Liu, J. S. Chen, M.-A Nicolet, V. Arbet-Engels, K. L. Wang, “Nanocrystalline Ge in SiO_2 by annealing of $\text{Ge}_x\text{Si}_{1-x}\text{O}_2$ in hydrogen”, *Applied Physics Letters*, Vol. 62, pp. 3321-3323, 1993.

[3.15] Gianni Taraschi, Sajan Saini, Wendy W. Fan, Lionel C. Kimerling, “Nanostructure and infrared photoluminescence of nanocrystalline Ge formed by reduction of $\text{Si}_{0.75}\text{Ge}_{0.25}\text{O}_2/\text{Si}_{0.75}\text{Ge}_{0.25}$ using various H_2 pressure”, *J. Appl. Phys.*, Vol. 93, No. 12, pp.9988-9996, 2003.

[3.16] A. Rodriguez, M. I. Ortiz, J. Sangrador, T. Rodriguez, M. Avella, A. C. Prieto, A. Torres, J. Jimenez, A. Kling, C. Ballesteros, “Comparative study of the luminescence of structures with Ge nanocrystals formed by dry and wet oxidation of SiGe films”, *Nanotechnology*, Vol. 18, p.065702, 2007.

[3.17] V. V. Afanas'ev and A. Stesmans, ” Energy band alignment at the (100) Ge/HfO_2

interface”, *Applied Physics Letters*, Vol. 84, pp. 2319-2322, 2004.

[3.18] T. C. Chang, S. T. Yan, P. T. Liu, C. W. Chen, S. H. Lin, and S. M. Sze, ”A novel approach of fabricating Germanium nanocrystals for nonvolatile memory application”, *Electrochemical and Solid-State Letters*, Vol. 7, pp. G17-G19, 2004.

[3.19] Scott K. Stanley, Shawn S. Coffee, John G. Ekerdt, “Interactions of germanium atoms with silica surface”, *Applied Surface Science*, vol. 252, pp.878-882, 2005.

[3.20] V. Ioannou-Souglidis, A. G. Nassiopoulou, “Investigation of charging phenomena in silicon nanocrystal metal-oxide-semiconductor capacitor using ramp current-voltage measurements”, *Journal of Applied Physics*, Vol. 94, pp. 4084-4087, 2003.

[3.21] M. K. Bera, S. Chakraborty, R. Das, G. K. Dalapati, S. Chattopadhyay, S. K. Samanta, W. J. Yoo, A. K. Chakraborty, Y. Butenko, L. Siller, M. R. C. Hunt, S. Saha, C. K. Maiti, “Rapid thermal oxidation of Ge rich Si_{1-x}Ge_x heterolayers”, *J.Vac. Sci. Technol. A*, 24(1), pp.1323-1329, 2006.

[3.22] D. R. Lide, *Handbook of Chemistry and Physics*, 81st Edition, 2002.

[3.23] Achyut Kumar Dutta, “Visible photoluminescence from Ge nanocrystal embedded into SiO₂ matrix fabricated by atmospheric pressure chemical vapor deposition.” *Applied Physics Letters*, Vol. 68, pp. 1189-1191, 1996.

[3.24] C. Busseret, A. Souifi, T. Baron, S. Monfray, N. Buffet, E. Gautier, M. N. Semeria, “electronic properties of silicon nanocrystallites obtained by SiO_x (x < 2) annealing”, *Materials Science and Engineering C*, 19, p237–241 ,2002.

Chapter 4:

[4.1] Y. Yang, A. Purwar and M. H. White, “Reliability considerations in scaled SONOS nonvolatile memory devices”. *Solid-State Electronics*, Vol. 43, pp.2025-2032, 1999.

[4.2] C. H. Tu, T. C. Chang, P. T. Liu, H. C. Liu, S. M. Sze, C. Y. Chang, “Formation of germanium nanocrystals embedded in silicon-oxide-nitride layer”, *Applied Physics Letters*, Vol. 89, Art. No. 052112, 2006.

[4.3] C. Lee, T. H. Hou, E. C. Kan, “Nonvolatile memory with a metal nanocrystal/nitride heterogeneous floating gate”, *IEEE Trans. Electron Devices*, Vol. 52, No.12, pp. 2697-2702, 2005.

[4.4] S. K. Kang, B. G. Min, J. J. Kim, D. H. Ko, H. B. Kang, C. W. Yang, M. H. Cho, “ Interfacial reactions between WN_x and poly Si₆Ge_{1-x} films”, *J. Appl. Phys.*, Vol.

Chapter 5:

- [5.1] T. Sugizaki, M. Kobayashi, M. Ishidao, H. Minakata, M. Yamaguchi, Y. Tamura, Y. Sueivama, T. Nakanishi and H. Tanaka, "Novel Multi-bit SONOS Type Flash Memory Using a High-k Charge Trapping Layer", *Digest of Technical Papers - Symposium on VLSI Technology*, pp. 27-28, 2003.
- [5.2] Y. N. Tan, W. K Chim, B. J. Cho and W. K. Choi, "Over-erase phenomenon in SONOS-type flash memory and its minimization using a hafnium oxide charge storage Layer", *IEEE Trans. Electron Devices*, Vol. 51, pp. 1143-1147, 2004.
- [5.3] Y. Q. Wang, J. H. Chen, W. J. Yoo, Y. C. Yeo, S. J. Kim, R. Gupta, Z. Y. L. Tan, D. L. Kwong, A. Y. Du, N. Balasubramanian, "Formation of Ge nanocrystals in HfAlO high-*k* dielectric and application in memory device", *Applied Physics Letters*, Vol. 84, pp. 5407-5409, 2004.
- [5.4] X. B. Lu, P. F. Lee, J. Y. Dai, "Synthesis and memory effect study of Ge nanocrystals embedded in LaAlO₃ high-*k* dielectrics", *Applied Physics Letters*, Vol. 86, p. 2031111, 2005.
- [5.5] P. F. Lee, W. L. Liu, Z. T. Song, J. Y. Dai, "Ge nanocrystals embedded in Hf-aluminate high-*k* dielectrics for floating gate memory application", *Proceedings of SPIE - The International Society for Optical Engineering*, v 5650, *Micro- and Nanotechnology: Materials, Processes, Packaging, and Systems II*, p. 150-155, 2005.
- [5.6] A. C. Rastogi ,R. N. Sharma, "Structural and electrical characteristics of metal-insulator-semiconductor diodes based on Y₂O₃ dielectric thin films on silicon" , *J. Appl. Phys.*, Vol. 71, pp.5041-5052, 1992.
- [5.7] J. Kwo, M. Hong, A. R. Kortan, K. T. Queeney, Y. J. Chabal, J. P. Mannaerts, T. Boone, J. J. Krajewski, A. M. Sergent, J. M. Rosamilia, "High ϵ gate dielectrics Gd₂O₃ and Y₂O₃ for silicon", *Applied Physics Letters*, Vol. 77, pp. 130-132, 2000.
- [5.8] A. A. Dakhel, "Characterisation of oxidised erbium films deposited on Si(1 0 0) substrates", *Materials Chemistry and Physics*, 100, pp. 366–371, 2006
- [5.9] D. Xue, K. Betzler, H. Hesse, "Dielectric constants of binary rare-earth compounds", *J. Phys.: Condens. Matter*, 12, pp. 3113–3118, 2006.
- [5.10] F. H. Ko, H. C. You, T. F. Lei, "Sol-gel-derived double-layered nanocrystal memory", *Applied Physics Letters*, Vol. 89, p. 252111, 2006.

[5.11] G. D. Wilk, R. M. Wallace, J. M. Anthony, "Hafnium and zirconium silicates for advanced gate dielectric." *J. Appl. Phys.*, Vol. 87, No.1, pp.484-492, 2000.



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論文題目：

利用矽鍺氧與矽鍺氮薄膜形成鍺奈米點在非揮發性記憶體應用之研究

Study on Formation of Ge Nanocrystal using SiGeO and SiGeN layer for Nonvolatile Memory Applications