Formation of silicide films in advanced silicon devices using excimer pulsed laser annealing

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**FORMATION OF SILICIDE FILMS IN ADVANCED
SILICON DEVICES USING EXCIMER PULSED LASER
ANNEALING**

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
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Statement of Originality

I hereby certify that the content of this thesis is the result of work done by me and has not been submitted for a higher degree to any other University or Institute.

7 April 05
Date

Chow Fong Ling
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SUMMARY

This research project studies the formation of Co silicides by KrF excimer pulsed laser annealing for possible applications to Si technologies. Capping layer such as Ti and TiN, which acts as a protective layer, was used to study the optical coupling effect of laser-annealed Co silicide. For each type of the capping layer, pre-amorphization implantation (PAI) of the Si substrate was incorporated into Co/Si systems to examine the impact of PAI on laser-annealed Co silicide. The study of single-pulsed laser thermal annealing (LTA) over a fluence range of 0.2 to 0.7 J/cm² was carried out. Using a determined optimum annealing condition established by the single-pulsed LTA, the study was extended to multiple-pulsed laser annealing at low fluence of 0.2 to 0.3 J/cm² to enhance the silicide formation while maintaining the silicide thickness. The formation of Co silicide by different annealing conditions was envisaged, and all the possible growth mechanisms of Co silicide have been discussed. LTA on Co (13 nm)/Si and Co (8 nm)/Si systems without capping layer was carried out for comparison.

It has been found that the formation of Co silicide can be strongly influenced by the presence of Ti cap. If high concentration of Ti is present in an intermix (or molten phase) of Co and Si, the thermodynamic of the growth mechanisms can be transformed from crystallization to amorphous phase formation. Whereas for the laser-annealed TiN/Co/Si system, the TiN is robust enough to remain intact over a wide range of fluence of 0.2 to 0.7 J/cm² for single-pulsed LTA. For single- and multiple-pulsed LTA, TiN still stays intact but degrades with the presence of severe ripple-like surface. Formation of pinholes has taken place for higher number of laser pulses. It has been found

that the TiN layer is able to endure the laser induced thermal shock prior the formation of pinholes. After stripping away the TiN layer, it has been found that the TiN capping has induced pinhole formation in the formed Co silicide for higher number of laser pulses. Undesirable factors such as severe ripple effect on the Co silicide surface, pinhole formation, presence of different metastable phases with different number of laser pulses, or/and laser-induced stress in Co silicide have led to a high sheet resistance observed from the laser-annealed Co silicide. Due to the difference in the optical coupling of the capping layers, the melting threshold of the Co/Si system is strongly dependent on the presence of the capping layer. In addition, the PAI layer in the Co/Si system is capable of promoting silicidation, and has shown thicker silicide formation compatible to the Co/Si system without PAI for the same laser annealing condition. For those systems which have reached the melting threshold, the melt depth is proportional to the laser fluence.

For the Co/Si system without any capping layer, it has been found that the native oxide still remained intact without hindering the formation of Co silicide, even for a condition of high number of laser pulses or high fluence. The developed laser annealing recipe was implemented on a Co (8nm)/Si system in a 0.13 μm CMOS device technology. The measured electrical performance shows that the junction leakage and the diode performance of the laser annealed n/pMOSFETs are comparable to the conventional RTA-annealed Co-silicided devices. However, the sheet resistance has been degraded due to the formation of a thinner mixed phase Co silicide.

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Chapter 1 Introduction

1.1 Motivation

Silicides are compounds of silicon with the transition metal. Silicides films are used on diffusion, gates and local interconnects to reduce the series resistance of devices. The transition-metal silicides are, in general, good electrical conductors with resistivities comparable to metals and metal-metal alloys [1]. In advanced complementary metal oxide silicon (CMOS) technologies, the formation of silicide by self-aligned silicide (SALICIDE) has shown the capability of lowering the resistance of gate and source/drain regions and contact resistance, thus increasing the device performance, especially for shallow junction and short channel devices. This is because the device speed is greatly affected by the RC delay of the gate and the parasitic resistance of the source/drain. Furthermore, SALICIDE process avoids the use of additional lithography.

Of all the elements, the silicides of groups IVA, VA, and VIA, are called the refractory metal silicides, and the silicides of group VIII are known as near noble metal silicides. Refractory metal silicides which are also known as silicon-rich silicides such as TiSi_2 , NiSi , CoSi_2 , WSi_2 , TaSi_2 , and MoSi_2 [2].

The application of silicide to CMOS (see Figure 1-1-1) gives rise to low contact resistance of gate and source/drain. During the operation of CMOS transistor, a current enters the contact perpendicular to the wafer surface, and then travels parallel to the surface in order to reach the channel. The parasitic series resistance, R_s , of the current path from the contact to the edge of the channel can be explained by

$$R_s = R_{co} + R_{sh} + R_{sp} + R_{ac} \quad (1.1)$$

Figure 1-1-1 Series resistance in CMOS.

where R_{co} is the contact resistance between the metal and the source/drain region, R_{sh} is the sheet resistance of the bulk region of the source/drain, R_{sp} is the resistance of the current lines crowding near the channel end of the source, and R_{ac} is the accumulation layer resistance.

The fabrication of integrated circuit involves a large number of processing steps. Hence, the silicide must be stable throughout these processing steps especially when they are subjected to several temperature treatments. Therefore, a silicide must fulfill some requirements for the purpose of gate and interconnection application.

Silicide should have low contact resistance, minimal silicon consumption, minimal junction penetration and no lateral diffusion. Lateral diffusion during silicide formation is related to interactions that span beyond the confined dimensions and is associated with the dominant diffusing species during the silicide formation [3]. A silicide-silicon interface that is not well defined could lead to early breakdown of the devices when bias is applied due to the concentration of the electric field at the sharper nodes at the interface. The sharpness of the interface is determined mostly by the cleanliness of the

silicon surface prior to metal deposition. Apart from it, the stability of the silicide on a doped substrate at high temperature, especially during silicide formation or dopant activation need to be considered [2, 4].

As semiconductor device dimensions continue to decrease, the main challenge in the area of silicide formation involves decreasing the silicide thickness while maintaining low contact silicide sheet resistance. Two of the most important properties of a silicide are sheet resistance and its effect on the junction leakage. When the silicide thickness reaches 30 nm and below for 0.13 μm devices, the second rapid thermal annealing (RTA) process window for both of these properties becomes narrower. Above a certain thermal budget the silicide agglomerates, causing the sheet resistance to increase. However, a minimum thermal budget is required for the formation of a smooth silicide/Si interface while maintaining good junction leakage [5].

Henceforth, a novel approach employing laser thermal processing (LTP) to produce CoSi_2 is studied. LTP provides several advantages compared to RTP. The use of laser irradiation, which deposits most of its energy near the sample surface, allows the reaction temperature for silicide formation and growth to be reached in the localized region of the irradiation, without the need of heating the entire wafer. In addition, the laser induced melt depth can be used to control the silicide thickness [3]. Besides, the composition of the silicide layer can be varied by varying the laser fluence. Moreover, the fast cooling rates ($\sim 10^{10}$ K/s) allow the formation of highly metastable phases, which is not obtainable in conventional annealing [6, 7]. However, there are some disadvantages of using LTP. The instability of laser energy might not give rise to reproducible results. The integration issues with the application of

LTP in forming the transistor are needed to be resolved [8]. Besides the LTP is not widely used in mass production due to its slow throughput.

1.2 Objectives

The objective of this project is to study the growth mechanisms of pulsed laser-annealed Co silicide on blanket Si substrate. On top of this objective, the capping layer which has been adopted as a protection layer [9, 10] or/and optical coupling layer [11] was used to study its effect in the laser-annealed Co silicide. Since the amorphous Si has a lower melting temperature compared to crystalline Si, it can be used to control the silicide thickness. Besides, it has been reported that the amorphous Si has improved the performance of silicide in rapid thermal annealing [12, 13] and laser thermal processing [14]. Hence, the purpose of this project also includes the study of the PAI effect in the laser-annealed Co silicide. The next objective is to form an ultra-shallow silicide for future CMOS application by optimizing the laser annealing condition. In order to compare the performance of silicidation for the cap/Co/Si system, a laser-induced silicidation on Co/Si system without capping layer was carried out too. Ultimately, the goal is to study the silicide formation in the device structures by applying the recipe which has been developed in the study of blanket substrate.

1.3 Major Contributions and Organization of Thesis

The present work was initiated by the need to understand the operation for excimer laser and the interactions of laser with matters. The properties of materials such as thermophysical and optical property were investigated for the purpose of simulation and the understanding of silicide formation during the

pulsed-laser annealing. The Simulation of Laser Interactions with Materials (SLIM) was performed so as to provide an estimation of temperature distribution profiles. An excimer single-pulsed laser annealing in a range of energy density of 0.2 to 0.7 J/cm² and multiple-pulsed laser annealing in low energy density of 0.2 to 0.3 J/cm² were implemented. In this project, Ti-capped and TiN-capped samples were prepared. The effects of capping layer which acts as a protection layer and optical coupling on the laser-annealed silicide film are studied. The effect of pre-amorphization implantation (PAI) layer is studied too. PAI and non-PAI study are carried out for each type of capping layer for the Co (13 nm)/Si system. The optimum process recipe for silicide formation is determined by investigating the effect of laser-induced silicidation for different laser fluences and different number of laser pulses.

This was followed by the study of silicidation for non-capped Co/Si system. In this part, 13 nm and 8 nm of Co have been studied. Thinner Co (8 nm) has been included in the experiments in order to study the effect of laser-induced silicidation on different thickness of Co.

To understand the growth of Co silicide by laser annealing, characterization tools like X-ray diffraction (XRD) was used to study the crystalline structure of phase formation. The morphology stability study was carried out by investigating the sheet resistance measurement. In addition, the surface topography was studied by using atomic force microscopy (AFM) and scanning electron microscopy (SEM). To study the depth profile and the atomic concentration distribution of the samples, Auger electron spectroscopy (AES) was performed. In order to gain more insight into the growth mechanisms for the laser-annealed silicides, transmission electron microscope

(TEM) was carried out. The recipes and conditions that have been developed were applied to test pattern by carrying out the electrical characterization. Parameters such as sheet resistance from Kelvin structure and leakage current from diode were measured.

The thesis is organized into eight chapters. Literature review on silicide will be reported in Chapter two. Next, Chapter three presents the principle of laser physics and laser-material interactions. The experimental setup and methodology adopted in the project will be discussed in Chapter four. This is followed by Chapter five showing the simulation results of the temperature profiles in Co/Si using SLIM software. The results of laser-annealed Ti-capped Co/Si sample and TiN-capped Co/Si sample are discussed and explained in Chapter six and seven, respectively. The findings of Co/Si sample without capping will be shared in Chapter eight. The application of the developed laser-annealed recipe and conditions to Si devices are discussed and the electrical performance of the silicided devices are presented in Chapter nine. Finally, Chapter ten will conclude the project and makes some recommendations.

Chapter 2 Literature Review

2.1 Silicidation

Silicides layer can be formed by solid-state reaction between a metal and Si or by co-depositing the metal and Si [15]. The solid-state reaction is used in a self-aligned silicide process and the co-deposition method is used in polycide process. The solid-state reaction is produced by subjecting the as-deposited metal film to a thermal treatment, which is called annealing where the reaction between the film and substrate will be promoted.

There are two types of annealing, i.e. steady state annealing and transient annealing [16]. For example, rapid thermal processing is a steady state annealing method. It utilizes tungsten-halogen lamps to provide thermal annealing. In transient type annealing, a pulse of energy is applied to the sample, and the temperature across the sample varies as a function of time. Hence, the physical process known for solid phase interactions do not necessarily apply in pulsed laser annealing. One of the most obvious deviations of metal-silicon interactions under transient conditions from those under steady state conditions is the metastability of the reaction products.

Figure 2-1-1 illustrates silicide and polycide process. For silicide process, after the fabrication of gate and source/drain junctions, a metal is deposited. The deposition of metal can be done using DC magnetron sputtering. The first annealing is carried out to form silicides. As there is no formation of silicide on the oxide area, the wafers are chemically wet etch to strip the unreacted metal to prevent bridging between the gate and source/drain. In order to lower the silicide resistivity completely, a second annealing is implemented.

In the polycide process, the gate polysilicon is deposited and doped by ion implantation. Next, a silicide is formed by co-sputtering metal and silicon and this is followed by deposition of insulator. The gate stack which comprises the polysilicon, silicide, and top insulator, is subsequently patterned. Then, sidewalls are formed by using chemical vapor deposition. Eventually, the silicide on the source/drain can be formed by using self-aligned process because the silicide is aligned with the gate polysilicon without using any additional masks.

Step	Salicide Process	Polycide Process
I.	<ul style="list-style-type: none">Fabrication of gate and S/D	<ul style="list-style-type: none">Fabrication of gateCo-sputtering metal & SiDeposition of insulator
II.	<ul style="list-style-type: none">Metal deposition	<ul style="list-style-type: none">Sidewall formation
III.	<ul style="list-style-type: none">1st annealingWet etch	<ul style="list-style-type: none">S/D formation
IV.	<ul style="list-style-type: none">2nd annealing	<ul style="list-style-type: none">Self-aligned silicide formation on S/D

Figure 2-1-1 Schematics of salicide process and polycide process.

2.1.1 Steady state thin film reactions

Under steady-state annealing conditions, transition metals react uniformly with Si single crystal substrates when no significant amounts of impurities are present. There are two types of silicide formation mechanism: diffusion-controlled growth and nucleation-controlled growth [17]. A flat interface over many atomic spacings between silicide and substrate can be observed in diffusion-controlled growth of silicide whereas silicide which is formed by nucleation-controlled generally has a non-uniform interface.

Steady state thin film reaction normally obeys phase diagrams. Some of the binary metal-silicide phases present as detectable growth phases under steady state annealing conditions. When the metal layer has been totally consumed in forming the first phase, a second phase that is present in the phase diagram, will form at higher temperatures or longer annealing times [17].

Theory of Thermodynamics

The basic thermodynamic concepts are required for a fundamental appreciation of phase diagrams and phase transformations. It allows the prediction of whether an alloy is in equilibrium. For transformations that occur at constant temperature and pressure, the relative stability of a system is determined by its Gibbs free energy (G). The Gibbs free energy of a system is defined by the equation

$$G = H - TS \quad (2.1)$$

where H is the enthalpy, T the absolute temperature, and S the entropy of the system. The enthalpy is a measure of the heat content of the system and is given by

$$H = E + PV \quad (2.2)$$

where E is the internal energy of the system, P the pressure, and V the volume.

The internal energy arises from the total kinetic and potential energies of the atoms within the system. The entropy (S) is a measure of the randomness of the system. A system is said to be in stable equilibrium if it has the lowest possible value of the Gibbs free energy [18].

2.1.1.1 Salicide and process issues

TiSi₂

Titanium disilicide (TiSi₂) has been widely used due to its low resistivity and high thermal stability. TiSi₂ is a polymorphic material and may exist either as a high resistivity (~60-90 $\mu\Omega\text{cm}$) base-centered orthorhombic C49 phase or a low resistivity (~15-20 $\mu\Omega\text{cm}$) face-centered orthorhombic C54 phase. The formation process requires two rapid thermal annealing steps with the first one falls between 550°C and 700°C, where C49 phase TiSi₂ forms in N₂ ambient (~30s). Then C49 phase transforms into C54 phase with a second annealing at temperatures greater than 750°C. During formation of TiSi₂, the major moving species is Si. As this would cause bridging between the gate and source/drain especially at high temperature, hence the annealing is carried out in N₂ ambient. Nitrogen can diffuse into the Ti between the contact forming TiN and blocks the lateral diffusion of Si. A second annealing is performed at a higher temperature in order to transform to the low resistance C54 phase [1, 15].

The formation of TiSi_2 is strongly affected by substrate doping. This is because Ti-dopant compounds at the TiSi_2/Si interface is likely to retard the TiSi_2 formation. Besides, cavities and voids at the TiSi_2/Si interface are formed after TiSi_2 formation by reacting Ti with BF_2 -implanted Si substrates [19]. As the gate lengths are scaled down to sub-0.25 μm , conversion of C49 to C54 phase becomes increasingly difficult as agglomeration of TiSi_2 occurs during phase transformation at high temperature. This is because the number of nucleation sites (i.e. triple grain boundaries) has decreased when the polysilicon linewidth reduces, and this effect is called “fine-line effect” [3, 20].

CoSi_2

Cobalt disilicide has attracted a lot of attention in sub-micron technology recently because of its superior characteristics. In addition having low resistivity (10-18 $\mu\Omega\text{ cm}$) and excellent chemical stability, Co silicide has lower linewidth dependence of R_s and higher post heat cycle immunity than Ti silicide. CoSi_2 has a face-centered cubic CaF_2 structure with only a $\sim 1.2\%$ lattice mismatch with Si which makes CoSi_2 an epitaxial silicide layer on Si substrate [21].

In the standard process, three silicides phases form during rapid thermal annealing of samples consisting of Co thin films deposited on Si substrates i.e. Co_2Si (the first phase to form with a heat of formation, $\Delta H_f = -9\text{ kcal/g atoms}$), CoSi ($\Delta H_f = -12\text{ kcal/g atoms}$), and CoSi_2 (the last phase to form, with $\Delta H_f = -8.2\text{ kcal/g atoms}$) [22]. It has been shown that Co_2Si and CoSi form according to the diffusion controlled mechanisms. Barge *et al.* reported that Co_2Si and CoSi form simultaneously during annealing at low temperatures when a thick

Co films begins to react with a (100) Si substrate [23, 24]. CoSi_2 starts to grow at temperatures of around 400 – 500°C. The kinetics of CoSi_2 growths are characterized by diffusion- and nucleation-controlled mechanisms [20, 25]. The general method to form polycrystalline CoSi_2 is carrying out the first RTA in N_2 ambient in which the wafer will be rapid thermal annealed at around 500°C to form CoSi . After removing the capping and unreacted metal layers, the wafer is subjected to a second RTA above 700°C in N_2 ambient to transform CoSi to CoSi_2 in order to lower the resistivity further. A minimum silicide lateral growth is expected during CoSi_2 formation because Co is the dominant moving species in Co_2Si and CoSi_2 formation [26, 27, 28].

As device dimensions continue to shrink, there will be increasing demand for shallow, uniform silicides. Therefore, there have been studies reporting the formation of epitaxial CoSi_2 as CoSi_2 has low lattice mismatch with Si. CoSi_2 has the CaF_2 structure with lattice parameter $a=5.365 \text{ \AA}$ at room temperature and this is about 1.2% smaller than that of Si with $a=5.431 \text{ \AA}$. Due to the large difference in the thermal expansion coefficient of CoSi_2 ($9.4 \times 10^{-6} \text{ K}^{-1}$) and Si ($2.3 \times 10^{-6} \text{ K}^{-1}$), the lattice match improves with the increasing of temperature [25]. Indeed, single-crystal, epitaxial silicides offer smoother interfaces, superior thermal stability against agglomeration, low resistivity, absence of fast grain boundary diffusion paths, and film uniformity. To form an epitaxial CoSi_2 film, several methods have been proposed involving solid-state interactions between Co and Si substrate, such as titanium-interlayer-mediated epitaxy (TIME), oxide-mediated epitaxy (OME), and high temperature sputtering (HTS). The success of direct formation of CoSi_2 as the first phase was believed to be due to the interlayer between Co and Si acting as

diffusion barrier, which decreases the Co concentration at the growth interface [29, 30, 31, 32, 33].

Although CoSi_2 has proven to be a good candidate of silicide for advance technology, Co consumes large amount of Si to form CoSi_2 compared to Ti, which is 25% greater than TiSi_2 [1]. The following shows the comparison of Si consumption for cobalt disilicide and titanium silicide [2, 19]:

Hence, cobalt silicide has certain limitation especially in ultra-shallow junction device and henceforth people have begun to study NiSi as a potential silicide candidate in future [19, 20].

A conventional Co silicidation using rapid thermal annealing is very sensitive to oxygen and moisture. The CoSi_2 formation is blocked by a thin interfacial native oxide. As a result, it gives rise to a high sheet resistance for narrower lines, overgrowth of silicide on the spacers, and rough silicide/Si interface. Besides, thinning effect of CoSi_2 layers at the edges adjacent to the oxide spacer and field oxide has been observed. This is caused by desorption of H_2O from the oxide as explained by Maex *et al.* [33].

2.1.1.2 Stability of silicide

The stability of silicide is important in order to prevent degradation of the silicide on the underlying devices. The stability of the silicides can be affected by a few factors: high temperature annealing can cause agglomeration of silicides on single crystal Si and this can result high sheet resistance and junction leakage. In addition, silicides enhanced polysilicon grain growth can occur during high temperature annealing and further leads to silicide inversion.

Layer inversion occurs when the silicide dissociates at the silicide/regrown Si interface and silicide grows at the silicide/polysilicon interface. As a result, metal redistribution and Si grain growth take place. This process is driven by the reduction of the polysilicon grain boundary and interface energy. Eventually, a surface layer of Si with the silicide underneath is formed [15]. Besides, discontinuous interfacial oxide between metal and Si gives rise to non-uniform silicide/Si interface, and this subsequently causes high sheet resistance [20].

2.1.2 Transient annealing

Pulsed laser annealing has been extensively adopted in growing thin films of silicides. Different types of metal thin films such as Au, Pt, Pd, Ti, Co, Mo, Ni and W [11, 34, 35, 36, 37, 38, 39, 40, 41, 42], have been used in formation of metal silicides by pulsed-laser annealing since in the earlier works. In comparison with rapid thermal annealing, pulsed laser annealing offers several advantages: it allows the local silicide formation without the need of heating the entire wafer. Besides, the composition of the silicide layer can be varied by varying the laser fluence. The fast cooling rates ($\sim 10^{10}$ K/s) allow the formation of highly metastable phases.

The formation of thin silicide layers by Q-switch Nd:YAG pulsed laser melting of films of Ni, Pd, or Pt on Si has been first demonstrated by Poate *et al.* [34]. Cellular structure can be observed in the solidifying phase due to constitutional supercooling of the melt. Tung *et al.* [42] has reported that the Ni and Co silicides formation on (100) and (111) Si has been improved by using Q-switched ruby laser. The interfacial instabilities and cellular structure can be suppressed by first carrying out furnace annealing to form NiSi_2 and

polycrystals CoSi_2 and subsequently melting the disilicide layers. Ultimately, epitaxial Ni and Co silicides are formed through liquid phase epitaxy growth.

In addition, XeCl pulsed laser irradiation has shown the capability of forming tungsten disilicide. Through the synthesis in vacuum environment, a low resistance ($5 - 10 \Omega$) and resistivity ($150 - 300 \mu\Omega\text{cm}$) of disilicide can be achieved. Similar to conventional RTA, laser annealing in N_2 atmosphere can accelerate the silicidation [39]. Luo *et al.* demonstrated that different phases can be produced by utilizing lower and higher energy density of KrF pulsed laser irradiation [39]. An amorphous overlayer was formed in Ni silicide/Ni germanosilicide when low energy fluence was used whereas cell formation occurred as a result of constitutional supercooling at high energy fluence [39]. By using the pulsed laser annealing, the agglomeration structure for Ni/ $\text{Si}_{0.76}\text{Ge}_{0.24}$ and Ni/ $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ does not occur [39, 40]. Platinum was also studied to form platinum silicide films by using Nd:YAG pulsed laser annealing. The growth sequence of PtSi/Si evolving from Pt-Pt₂Si-Si, Pt-Pt₂Si-PtSi-Si, and Pt₂Si-PtSi-Si to PtSi-Si, can be examined by X-ray photoelectron spectroscopy (XPS) as the result of the diffusion reaction in the bilayers with an increase of laser annealing time [43].

The application of laser thermal processing has also been extended to device study [14]. It has been used to eliminate the fine line effect that occurs during the Ti silicide transformation from C49 to C54 phase. A fine and nano-grain of C49 can be achieved by using single pulsed laser annealing, in which subsequently the formation temperature of C54 TiSi_2 can be lowered [44]. Furthermore, a C40 TiSi_2 template forms after LTP and this facilitates the

transformation to C54 phase at low temperature RTA without presenting any linewidth dependent phenomenon [45].

2.2 Improvement of Silicide Formation

2.2.1 Pre-amorphization implantation

PAI is a process where the surface layer of silicon is amorphized through high-energy ion implantation like Si, Ge or As prior to metal deposition. In solid-state reaction, the pre-amorphization layer has proved to provide thermal stability of TiSi_2 and CoSi_2 formation on silicon and polysilicon [15, 47, 48, 49]. Issues such as lateral voids, dopant segregation, thermal agglomeration, and increase of resistance on narrow linewidth are suppressed by using the PAI technology. This is because the amorphous Si raises the free energy of the system since the amorphous Si has higher free energy compared to crystalline Si. This increases the driving force for the nucleation of the new phase. Eventually, it results in smaller silicide grains and lower the temperature of silicide formation. Maa *et al.* has used amorphous Si to reduce Si consumption during cobalt silicide formation [50].

The melting temperature of amorphous Si is 200 K lower than that of crystalline Si [51, 52]. It is thermodynamically unstable in the presence of crystalline Si and tends to regrow epitaxially, layer by layer, on the underlying crystal. The PAI layer can be utilized to control the silicide depth. Liu *et al.* has achieved a well-controlled silicide thickness and a smooth silicide/Si interface without agglomeration by applying germanium pre-amorphization [48]. Furthermore, a low sheet resistance of C54 TiSi_2 film can be obtained

with a low thermal budget using pre-amorphization layer [13, 48]. In laser thermal processing, the use of amorphous Si layer has shown success in silicide formation [14, 53]. The application of PAI has alleviated the fine-line effect incurred by TiSi_2 as gate length goes below $0.25\mu\text{m}$. A thicker silicide over the gate than over the source and drain is produced by using pulsed laser radiation. Henceforth, this has facilitated the phase transformation from C49 TiSi_2 to low resistivity C54 TiSi_2 . In addition, there is a study proposing the usage of PAI to suppress lateral encroachment and void-generation during formation of cobalt silicide [54].

The application of PAI has been extended into the formation of p^+/n ultra-shallow junction [55, 56]. Spike RTA and laser annealing have been carried out to compare the dopant distribution profiles. The results show that a step-like dopant profile can be obtained with a single-pulsed laser irradiation. This is because there is possibility to melt the whole amorphous layer without melting the underlying crystalline substrate and the entire pre-amorphized layer can be recrystallized to single crystalline (100) Si after laser annealing [56]. Although the amorphous layer in pre-amorphized silicon can be completely annealed by laser, the end-of-range damages were not sufficiently annealed. The supersaturation of interstitial defects in end-of-range region enhance the diffusion of boron during a post-laser processing anneal. Henceforth, a lower energy and dose of implantation can be adopted to form ultra-shallow junctions [57].

2.2.2 Capping layer

The use of capping layer can be used to improve the thermal stability of silicide/polysilicon structures. It can increase mechanical constraint against

deformation. Furthermore, the capping layer can reduce surface energy and reduce lateral diffusion of silicon along refractory metal surfaces and grain boundaries. Pfister *et al.* [58] has achieved a low sheet resistance polysilicon gate with low leakage source/drain junctions while preventing the silicide from bridging over the oxide sidewall spacers between the gate and source/drain regions by using TiN strapped layer. Apart from it, capping layer can minimize oxygen contamination during annealing. Generally, Ti or TiN layer is used as capping layer for cobalt silicidation since they are effective getter for H₂O and O₂. Capping layer can be divided into two groups, reactive and nonreactive capping. Examples of nonreactive capping are TiN, Mo and W, whereas Ti is a reactive capping [59].

Titanium Nitride

TiN is a hard, dense, refractory material and it has high thermal and electrical conductivity [60]. It is very hard and has a very high melting point. The bond energy of TiN is 13.24 eV [61]. It has a poor thermal expansion relative to silicon. Hence, stress is resulted if thick films are employed. TiN film is face-centered cubic where nitrogen fits into the gap in the Ti crystal structure. The structure changes from hexagonal to face-centered cubic as the amount of nitrogen is increased. The incorporation of nitrogen in TiN has made the characteristic of golden appearance. Although TiN has the property of high hardness and corrosion resistance, it is susceptible to presence of impurities particularly O₂, which tends to distort its crystal structure. Its high reflectivity in the infrared region makes the TiN film as a heat mirror [62].

Despite the fact that TiN can protect the surface by preventing impurities such as O₂ and H₂O from interaction with Co/Si, it cannot suppress

the thermal desorption of moisture from the adjacent oxide. Maex *et al.* reported that the sheet resistance of Co silicided poly-Si lines with TiN cap shows linewidth dependence on the first RTP temperature and edge-thinning effect is observed [33].

Titanium

Titanium is a polymorphic metal, which exists in two allotropic modifications with different crystal lattices. The low-temperature modification (α -titanium) has a close-packed hexagonal lattice. The high-temperature modification (β -titanium) has a body-centered cubic lattice, which is stable at temperatures above 882.5°. The temperature of the allotropic transformation depends on the degree of purity of the metal. Generally, the transformation occurs between 865 - 900°C in the presence of impurities. Titanium is highly reactive at high temperatures and it easily interacts with oxygen above 550°C [63].

Ti has not only been used as diffusion barrier to form epitaxy silicide, but also as a protection layer in cobalt silicidation [64]. Ti is a reactive material which not only can getter O₂ and H₂O either from ambient or thermal desorption, but also capable of reducing the interfacial Si oxide. This is because Ti has a strong affinity to oxygen. Any native oxide or residual will be reduced by the reaction $\text{Ti} + \text{SiO}_x \rightarrow \text{TiO}_2 + \text{Si}$. Detavernier *et al.* [30] reported that Ti from the capping layer diffuses through the Co layer probably by fast grain boundary diffusion and reduces the interfacial SiO₂ into the form of Co_xTi_yO_z. In addition, the Ti on top of Co can transform into TiO_xN_y compound in N₂ ambient so there is unlikely a further formation of SiO₂. However, an optimized Ti layer thickness is necessary to be used in order to

reduce the loss of Co for silicidation as well as limiting of interaction with Si oxide and nitride [59].

2.3 Summary

Metal silicides have been used for interconnects, gate and source/drain contacts in order to reduce the series resistance and increase the device performance. The silicidation can be taken place by adopting steady state annealing or transient annealing. Steady state annealing obeys phase diagrams and takes place at constant temperature and pressure. In contrast, transient annealing is carried out by irradiating laser pulse. Henceforth, transient annealing allows localized silicidation without the need of heating the whole wafer. Among the metal silicides, cobalt disilicide has been widely used due to the lowest resistivity and good thermal stability. Besides, its cubic crystalline structure has good lattice match with Si and an epitaxial CoSi_2 can be grown on Si substrate. However, the Co silicidation is very sensitive to oxygen and moisture, hence a capping layer has been used for protection during rapid thermal annealing. The Si consumption for Co is the highest among Ti, Ni, and Co. Nevertheless, a few methods have been developed to overcome the issues. The capping layer such as Ti and TiN have been used to protect Co silicidation. The amorphous Si layer produced by the PAI has a lower melting point than crystalline Si and can be used to control the silicide thickness. Therefore, PAI has been proposed in this study to control Co silicide thickness during LTA. Furthermore, the PAI has shown the capability in preventing the layer inversion and agglomeration.

Chapter 3 Laser & Its Interaction with Solids

3.1 Laser

LASER internationally stands for Light Amplification by Stimulated Emission of Radiation. Laser are devices that generate coherent radiation at the frequencies in the infrared, visible, ultraviolet and soft X-ray regions of the electromagnetic spectrum by using the stimulated emission of radiation. It can be operated in a variety of forms by using different laser materials, different atomic and molecular systems, and different kinds of pumping techniques. Examples of laser types are pulsed Nd:YAG, CO₂ gas laser, excimer laser, and others. Laser can be described as monochromatic waves with single frequency and highly coherent. It can operate either in continuous mode or pulsed mode depending on the excitation mode and the active medium of the laser [65, 66].

3.1.1 Basic principles of excimer laser

The term 'excimer' is short for 'excited dimer' where 'dimer' refers to a diatomic molecule. The amplifying medium of excimer laser is the excited molecules. The typical components of excimer are rare gas (e.g. He, Ne, Ar, Kr, and Xe), and halogen gas. The rare gas is inert, as it does not readily react with other atoms or molecules to form new molecules. When the atom is electronically excited by changing the orbital motion of electrons or by removing one, it can become highly reactive to other atoms or molecules in the vicinity. Henceforth, when the positively charged ions of rare gas approaches the negatively charged halogen (F, Cl, Br or I) that have an extra electron in their outer orbit, the excited rare gas and the halogen are likely to form a molecule.

Chapter 3 Laser & Its Interaction with Solids

During the process of energizing the amplifying medium, the Kr gas and F₂ gas are contained in a form of enclosure (laser cavity) and are pumped by passing an electric discharge through the medium itself. Collisional excitation of the gas mixture by energetic electrons produces excited krypton and fluorine atoms by reactions as follows:

Then the ions recombine to form an excimer through the three-body reaction

where A is an excited buffer gas atom (usually helium or neon). The process which the buffer gas atom takes up the excess energy is called harpooning reaction. The use of excited buffer gas atom is to ensure momentum conservation. The laser is emitted when the radiative transition between the excited state of a molecule and its ground state. During the radiative transition, the KrF^{*} forms the upper state population and KrF molecules form the lower state population. Since, the lifetime of the excited molecules is 5~15 nanosecond compared to KrF molecules, which is tens of femto-second, hence a population inversion is easily built between these two molecular states (see Fig. 3-1-1). Subsequently the laser action in rare gas excimer molecules takes place from B to X transition.

The potential energy of the excited molecule shows a dependence on the distance of the two atoms as can be seen in Fig. 3-1-1. When the nuclei come closer to form the excited rare gas halide molecule KrF, the KrF^{*} is unstable. After 5-15 nanoseconds of its formation, an ultraviolet (UV) photon is emitted

and puts the molecule into its ground state. After lasing, the unexcited atoms are strongly repulsive and weakly attractive. In other words, the ground state of a rare gas halide molecule essentially does not exist. Therefore, the repulsive state or weakly bound states makes an ideal lower level for a laser transition. In addition, to obtain a large probability of atom reactions that can form the excimers, a high pressure in the order of magnitude of several 100 kPa must be used.

The intensity distribution of excimer laser beam is in Gaussian pattern. The generation of this Gaussian laser beam is caused by the feedback of a laser amplifier by two mirrors forming the resonator inside the laser cavity [65].

Figure 3-1-1 Binding energy versus internuclear separation for the rare gas halide molecules KrF showing the B to X laser transition and the excited atomic levels of the rare gases responsible for the formation of the B-state [66].

3.1.2 Interaction of laser with materials

There are some features for application of laser radiation, where ordinary thermal radiation cannot be found. Laser is highly directional and

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coherent. It is capable of self-interference. The laser can be described as an electromagnetic radiation with the carrying of photon. Photons are absorbed in a solid through a process known as photoelectric effect in which a photon interacts with an electron by giving all its energy to the electron.

During the photoelectric process, absorption of light by matter occurs. The interaction of photon with matter depends on the energy states of its valence electrons. The electrons which are tightly bound to their orbital around the atomic nucleus respond weakly to the electromagnetic wave and mainly affect its phase velocity whereas free electrons can extract energy from the electromagnetic wave. The electron is ejected from the atom by the absorption of an x-ray. This loss of an electron leaves the atom in an excited state. After absorbing the energy, the energy is transmitted to the lattice. Sometimes, reflection can be occurred due to the reradiation of energy and this also depends on the property of the surface material.

The mechanisms of absorption of light can be described by the following relationship:

$$I(t) = I_0 \exp(-\alpha t) \quad (3.1)$$

where $I(t)$ is the intensity of light at depth t , I_0 is the incident intensity and α is the absorption coefficient.

The properties of light can be described in terms of complex refractive index, by the following equation.

$$\hat{n} = n + ik \quad (3.2)$$

where n is the ratio of the phase velocities in vacuum and in the material. The imaginary part k is extinction coefficient which describes the damping of the

light wave. The reflectivity R and the absorption coefficient α can be defined by factor n and k with the well-known relations where it applies for normal incidence.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3.3)$$

and

$$\alpha = \frac{1}{d} = \frac{4\pi k}{\lambda} \quad (3.4)$$

where d is the absorption length and λ is the wavelength of light.

In addition, a beam can be characterized by fluence or energy density in which its unit is in joules per square centimeter.

3.2 Pulsed Laser Induced Silicidation of Metal-silicon Bilayers

As compared to solid-state reactions between the as-deposited metal and silicon, a rapid heating and high quenching rates on the order of 10^{10} K/s can be achieved. The faster rate of cooling rate has given rise to the formation of metastable phases. The transformation of a sample through melting by a high heat pulse into its final form can be discussed in three aspects: heat flow, mass diffusion and molecular rearrangements (solidification) [35].

3.2.1 Heat flow

When the metal on top of silicon is exposed to laser, it can cause the melting of the film and part of the substrate depending on the energy of laser. The heat generation function is determined by the interaction of the laser radiation with the material and the subsequent transfer of the energy to the lattice. It can be hypothesized that the absorbed light is converted into heat

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instantaneously. For simplicity, the laser beam travels along the z -axis and is uniform in the x, y plane. The target sample is assumed to be homogeneous. Hence, the heat equation which depends on time and space is evolved as below:

$$\rho(T)C_p(T)\frac{\partial T(z,t)}{\partial t} = \frac{\partial}{\partial z}\left[K(T)\frac{\partial T(z,t)}{\partial z}\right] + \alpha(1-R)I_0(t)\exp(-\alpha z) \quad (3.5)$$

where T is the temperature, t is the time, ρ , C_p , K , and α are the density, specific heat, thermal conductivity, and the absorption coefficient of the sample, respectively. R is the reflectivity of sample.

In general, the surface thermal field induced by pulsed laser irradiation is not due to heat diffusion only; it also depends on the penetration depth of laser light itself. Therefore, the laser heating depends on the optical absorption length (α^{-1}) and heat diffusion length ($\sqrt{2D\tau}$), where D is the thermal diffusivity and τ is the interaction time i.e. the pulse length. The rate at which heat is dissipated in a solid is determined by the heat diffusivity $D=K/C_p\rho$. Fig. 3-2-1 shows schematic of temperature distribution in laser-irradiated sample where $\alpha^{-1} < \sqrt{2D\tau}$. The average temperature rise in this layer is given by

$$\Delta T = \frac{(1-R)I_0\tau}{C\rho(2D\tau)^{1/2}} \quad (3.6)$$

Figure 3-2-1 Temperature distribution in laser-irradiated Si in which the absorption distance α^{-1} is less than the heat diffusion length $\sqrt{2D\tau}$ [34].

Ultimately, the cooling rate determines the composition and structure of the irradiated material. The phase of the solidified layer is strongly affected by the solidification velocity. The velocity of solidification of the molten phase can be estimated as shown in Fig. 3-2-2. The heat liberated at the advancing interface is given by $\Delta H_m \rho v$, where ΔH_m is the enthalpy of melting. This heat is balanced by the heat flow ($K \frac{\partial T}{\partial z}$) into the substrate. The temperature gradient can be calculated to the first order by $T_m/(2D\tau)^{1/2}$ [34].

Figure 3-2-2 Schematic illustrating the velocity of the liquid-solid interface, which is determined by the balance between the latent heat liberated and its heat flow into the substrate.

3.2.2 Mass diffusion

With the nanosecond of pulsed laser annealing, the solid-state diffusion is negligible. However, if the laser energy density is high enough to cause the melting of the materials, the atoms in the melt can have high mobilities, corresponding to diffusivities on the order of $10^{-4} \text{ cm}^2/\text{s}$ as compared to $10^{-9} - 10^{-12} \text{ cm}^2/\text{s}$ in a solid. Therefore, from the kinematic point of view, the mass transport of atom in the liquid phase can take place over tens of nanometers. The diffusivities in liquids depend on composition as well as on the energy of

laser. For the case of a deposited metal on top of silicon, a rectangular distribution of concentrations is resulted after pulsed laser annealing [6, 34].

3.2.3 Solidification

The temperature gradient and laser pulse length can influence the recrystallization velocity. Eventually the undercooling of the melt determines the recrystallization velocity. The higher the undercooling, the larger the recrystallization velocity.

From the thermodynamic point of view, a large undercooling is needed to allow the crystallization. The presence of a nucleus is required before a new crystal can grow. When the solidification starts, the single crystal substrate serves as nucleus. For the formation of compound phase, nucleation must occur in the melt. The nucleation of given volume of liquid can be explained by free energy change. The free energy change associated with the formation of a small volume of solid has a negative contribution due to the lower free energy of a bulk solid, and a positive contribution due to the creation of a solid/liquid interface. Hence, the free energy change for a sphere of a radius r is

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \quad (3.7)$$

where r is the radius of nuclei, ΔG_v is the volume free energy and γ_{SL} is the solid/liquid interface energy. Figure 3-2-3 illustrates the free energy change associated with homogeneous nucleation of a sphere of radius r . To promote nucleation, larger amount of undercooling is necessary. As can be seen from Fig. 3-2-3 that for a given undercooling there is a r^* , which is associated with a maximum excess free energy. If $r < r^*$ the system can lower its free energy by

dissolution of the solid, whereas when $r > r^*$ the free energy of the system decreases if the solid grows.

Figure 3-2-3 The free energy change associated with homogeneous nucleation of a sphere of radius r .

During the solidification of LTA, the fast cooling rate freezes the phase at room temperature. Consequently, the phase remains thermodynamically metastable. Therefore, an amorphous or glass phases, layers of metastable polycrystalline phases, layers of metastable epitaxial phases or equilibrium phases can be obtained by changing the metal or composition or irradiation conditions. The later one can be varied by changing the pulse duration time, the energy density, or the substrate temperature during annealing.

3.2.4 Solid phase epitaxial regrowth

Solid phase epitaxial regrowth is a process where an amorphous overlayer on single crystal substrate is crystallized epitaxially at temperatures below the melting or eutectic point of the material. And this can be done by using furnace annealing or by long duration of laser pulses ($t > 10^{-3}$ s). Sometimes, a metal or silicide layer which serves as a transport medium is interposed between the amorphous and crystalline silicon in order to provide

driving force for the process. The higher free energy of the amorphous phase has facilitated the reduction of free energy of the system by recrystallization of the amorphous layer on the underlying substrate.

3.2.5 Liquid phase epitaxial regrowth

When the liquid layer has a composition corresponding to that of a solid compound whose lattice spacing matches the substrate, the heterogeneous nucleation of that compound is kinetically preferred. The substrate which acts as a template for the epitaxial regrowth has facilitate the liquid phase epitaxial regrowth. This has been demonstrated for the case of CoSi_2 and NiSi_2 . However, the crystal growth velocity is inversely proportional to the degree of undercooling. If the undercooling becomes large enough, an amorphous phase formation could be resulted.

3.3 Constitutional Supercooling

The freezing behaviour of liquids can be altered by the small amounts of substances in solution, e.g. alloys and impurities. The impurities tend to remain in the liquid instead of participating in freezing with the solvent atoms. As a result, the freezing point of the liquid is lowered and the crystals are purer than the liquid from which they grow. The cause of this behaviour is a difference in size between the atoms of solute and solvent. There is little difficulty in mixing such atoms together in liquid. But in the crystal when some of the atomic sites are occupied by solute and the others by solvent, an oversized or undersized solute atom is a source of localized distortion in the crystal round it, and the distortion adds to the free energy of the crystal. As a result, the concentration of solute in the crystal is reduced, relative to that of the

liquid in order to keep this extra free energy as small as possible; and the liquid must be cooled further before its own free energy matches that of the crystal so that the freezing point is thereby lowered.

An important consequence of this phenomenon is constitutional undercooling (or constitutional supercooling). An unstable solid-liquid interface can be resulted by the constitutional supercooling when the temperature gradient is positive. Suppose a small bulge forms. The solid there projects out into the more highly supercooled liquid and the rapid freezing of this enables it to grow more. Therefore, the effect of this is the formation of a cellular structure in the growing crystal as shown in Fig. 3-3-1. The growing bulge rejects solute at its sides. This produces a high concentration in the liquid near its base. The liquid remains unfrozen as the rest of the interface moves forward and convexities are thereby form at P and Q on the interface. Henceforth, these P and Q are starting points for other bulges.

Figure 3-3-1 Cellular structure of a crystal grown from an impure liquid; (a), (b), (c) formation (d) appearance of the crystal at the solid-liquid interface [67].

3.4 Explosive Crystallization

When a low energy density of pulsed-laser irradiated on a Si sample with an amorphous layer, the laser energy melts only a thin amorphous layer. When this liquid begins to solidify as polycrystalline Si, the latent heat released from the liquid raises the temperature of the resolidified polycrystalline Si above the melting temperature of Si. The new liquid is severely undercooled with respect to the polycrystalline Si. Hence, explosive crystallization occurs when the new liquid is quenched by the energy required to raise the temperature of the amorphous Si solid in front of the liquid. The difference of thermal conductivity between amorphous Si and crystalline Si has facilitated the explosive crystallization proceeding to the amorphous-crystal interface at very low energy density. As a result, a bi-layered structure consisting of coarse-grained polycrystalline Si and fine-grained polycrystalline Si (with the coarse-grained polycrystalline Si on top) is formed [52, 68].

3.5 Summary

An excimer laser is produced by energizing the amplifying medium, in which consists of Kr and F₂. A 248 nm of excimer laser can be described as a photon with energy of 5 eV. The interaction of laser with materials is through photoelectric process. During the process, the valence electron is ejected by extracting the energy from the photon. Subsequently, the energy is transmitted to the lattice. The optical properties of material can be described by the absorption coefficient, reflectivity, refractive index, and extinction coefficient. When a laser pulse is irradiated on the surface of a sample, the surface thermal field is not only due to the heat equation, but also the dependency of laser on

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the penetration depth. Generally, the light absorption distance is less than the heat diffusion length. When the laser is strong enough to cause the melting of materials, the diffusivity of the atoms is higher in the liquid phase than in the solid phase. Prior to solidification, undercooling of the melt normally takes place in order to start the nucleation. Segregation of impurities and constitutional supercooling can be observed for the solidification of an impure solution .

Chapter 4 Experimental Setup

4.1 Sample Preparation

4.1.1 Sample preparation of Co/Si System with capping on blanket substrate

First, 200 mm n-type Si (100) wafers were used as substrates. The resistivity of n-Si wafer is 3.3-40 ohm-cm. All the wafers received a standard RCA cleaning. Then a 45 nm of initial oxide was grown and stripped away. The purpose of the initial oxide is to getter the oxygen of the substrates. Fig. 4-1-1 shows the schematics of film stacks on a Si substrate. Five wafers have been prepared for blanket study:

1. Ti (12.5 nm)/Co (12 nm)/Si
2. Ti (12.5 nm)/Co (13 nm)/Si
3. Ti (12.5 nm)/Co (13 nm)/PAI (50 nm)/Si
4. TiN (20 nm)/Co (13 nm)/Si
5. TiN (20 nm)/Co (13 nm)/PAI (50 nm)/Si

The sample of Ti (12.5 nm)/Co (12 nm)/Si was used as the preliminary study of Ti-capped Co silicidation.

Figure 4-1-1 Schematics of as-deposited films on blanket Si substrate.

The implant condition to form the desired thickness of PAI can be found in ref. [69]. Monte Carlo technique was used to further confirm the implant conditions. The simulation was carried out using a UT-Marlowe

software and the results are shown in Appendix I. The input parameters of the simulation are dose and energy, which then determine the thickness of a PAI through the Monte Carlo simulation. For the formation of a 500 Å PAI layer, the wafers were implanted with Si⁺ to a dose of $1 \times 10^{15} \text{ cm}^{-2}$ at an energy of 20 keV. After that, a 155s of diluted hydrofluoric acid clean was carried out for all the wafers prior to a Co deposition to remove any native oxide on the blanket wafer. Then, a 12.5 nm of Co was deposited, followed by the deposition of capping layer (12.5 nm for Ti capping layer and 20 nm for TiN capping) in different chambers without breaking vacuum. A detailed description of the sputtering system will be provided in Section 4.3.

Cross sectional transmission electron microscopy of as-deposited film stacks

A cross sectional TEM (XTEM) was carried out to check the real thickness of the samples before laser annealing for the Ti/Co/Si and TiN/Co/Si sample with the 50 nm PAI layer (see Fig. 4-1-2). As can be seen from Fig. 4-1-2(a), the as-deposited films are polycrystalline since the grain structures can be observed. In addition to a bilayered structure (i.e., Ti (18 nm)/Co (16 nm)), there is about 5.5 nm of TiO_x thickness on the surface of the Ti layer. The growth of TiO_x on the surface of Ti is due to oxidation under the atmospheric ambient, since Ti is capable of gettering oxygen. Besides, amorphous interlayers (α) were formed in the as-deposited samples. It is believed that the intermixed amorphous layer (i.e. α -interlayer) between Co and Si was formed during the deposition of the first initial Co layer since the pedestal of the sample was always kept the Co deposition at room temperature, the Si bonds near the surface are broken by the diffusion of Co atoms since Co is the

dominant diffusive species during intermixing [47, 70]. Similar mechanism is believed to be responsible for the α -interlayer between Ti and Co seen in Fig. 4-1-2. Therefore, the TiO_x and the amorphous interlayers should not be taken into account in investigating the actual thickness of the as-deposited sample. This is also needed to be considered for other samples as well. In contrary, no oxide layer was observed on the TiN surface since TiN is an inert material. Hence, the real thickness of the as-prepared samples is listed in Table 4-1-1.

Figure 4-1-2 XTEM of a (a) Ti/Co/Si system with PAI layer and (b) TiN/Co/Si system with PAI layer. (α indicates amorphous phase)

Table 4-1-1 Summary of the thickness for capped Co/Si system with and without PAI.

Sample	Thickness observed from XTEM (nm)	Actual thickness (excluding TiO_x & α interlayer) (nm)
Ti/Co	18/16	12.5/13
Ti/Co/PAI Si	18/16/50	12.5/13/50
TiN/Co	20/16	20/13/50
TiN/Co/PAI Si	20/16/50	20/13/50

4.1.2 Preparation of Co/Si system without capping on blanket substrate

A wafer with a layer of 13 nm of Co without a capping layer was prepared for the purpose of comparison with those samples with a capping layer. Similarly, a diluted hydrofluoric acid clean was carried out prior the metal deposition. A thinner Co layer (8 nm) was sputtered in order to study the formation of thinner silicide layer.

Cross sectional transmission electron microscopy of as-deposited film stacks

The XTEM micrograph shown in Fig. 4-1-3 reveals that there is a ~1.7 nm of CoO_x formed on the surface of the as-deposited Co/Si samples. For the non-capping silicide study, two types of wafers were prepared and the thickness of each sample is tabulated in Table 4-1-2 after considering the amorphous interlayer.

Figure 4-1-3 XTEM of as-deposited Co (13 nm)/Si system.

Table 4-1-2 Summary of the thickness for a Co/Si system without PAI.

Sample	Thickness observed from XTEM (nm)	Actual thickness (excluding CoO _x & α-interlayer) (nm)
Co	16.2	13
Co	11.6	8

4.1.3 Preparation of Co/Si system without capping on patterned wafers

In this work, the wafers with test structures such as junction diodes and Kelvin structure were used for the electrical study. Three kinds of junction diodes were investigated, i.e., n+/p perimeter intensive diode, p+/n perimeter intensive diode, p+/n area intensive diode. The Kelvin structures that were used for sheet resistance measurement are n+ active and p+ active.

A 0.13 μm CMOS technology was adopted for the fabrication of the test structures on p-type (100) silicon substrate. The substrates were isolated by growing 400 nm shallow trench isolation (STI). The implant conditions for the formation of n+/p junction are As at 45 keV with dose of $3 \times 10^{15} \text{ cm}^{-2}$ and P at 30 keV with dose of $2 \times 10^{13} \text{ cm}^{-2}$. The p+/n junction is formed by implanting B at 3.5 keV with dose of $3 \times 10^{13} \text{ cm}^{-2}$. The junction depths of n+/p and p+/n junctions are 120 nm and 80 nm, respectively. Next, the wafers were cleaned by using diluted HF in order to strip away the native oxide. An 8 nm of Co layer was deposited using DC magnetron sputtering system. After the laser processing, the unreacted Co was chemically removed by using SC1 (chemical combination of NH₄OH, H₂O₂, and H₂O) prior to the electrical measurement. This is to prevent bridging between the test structures. The procedures of SC1 are as following:

1. NH₄OH:H₂O₂:H₂O with concentration ratio of 1:1:6 at 70°C.
2. Deionized water rinse.

Figures 4-1-4(a) and (b) show the schematics of a perimeter intensive diode and area intensive diode whereas Fig. 4-1-5 shows the schematic of a Kelvin resistor. For both n+ and p+ active Si of the Kelvin structures, two different linewidth, i.e., 0.15 and 0.5 μm were studied. The length of the Kelvin resistor is 220 μm .

Figure 4-1-4 Schematic of a (a) perimeter intensive diode and (b) area intensive diode.

Figure 4-1-5 Schematic of a Kelvin structure.

4.2 Pulsed Laser Annealing System

Excimer laser has superior features compared to other types of laser such as Nd YAG, solid state laser, ruby laser, and others. As excimer laser works in ultra-violet range, it has strong coupling with metallic surface. This is because excimer laser light contains a reduced coherence, primarily due to a large number of transverse modes, hence the interference effects at the surface during irradiation can be avoided. Laser which is highly coherent like ruby laser can produce surface with periodic ripple patterns. Hence, a KrF₂ excimer laser with a wavelength of 248 nm was selected for pulsed laser annealing experiments.

The laser system that was used in this project is Lambda Physik LPX220i as shown in Fig. 4-2-1. The system consists of three units - a laser workstation, a excimer laser unit and a separate control console. The control console houses a Unidex motion controller, stage amplifiers, a laser PC controller and a beam profiler PC. The doors of the workstation are protected by fail-safe interlock switches which disable the laser when they are opened. The excimer laser unit is a KrF₂ excimer laser with a wavelength of 248 nm at a repetition rate of 1Hz. Fig. 4-2-2 shows the details of the laser workstation. It consists of a laser delivering system and a sample stage. This laser delivering system utilizes a macro beam homogenizer to control the output spot size, in which the final laser beam area is 6.25 mm² (2.5 mm × 2.5 mm). It is equipped with control software, which can be used to control the number of irradiated pulses and movement of the stage automatically. During the laser irradiation, the system was operated at a repetition rate of 1 or 2 Hz. A single pulse laser

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annealing in a range of laser fluence (also called energy density) from low to high and multiple pulses at low fluence were used to implement the laser annealing.

The pulsed laser annealing was carried out in class 100 clean room. There was no nitrogen, argon or other inert gas purging during annealing. During the laser annealing experiment, a sample size that is roughly $1\text{ cm} \times 1\text{ cm}$ was prepared. Then the whole sample surface received a maximum coverage of laser spot in order to facilitate the subsequent characterization work. This was done by scanning the $2.5\text{ mm} \times 2.5\text{ mm}$ laser spot size on the area of interest. This approach is similar to the “step and scan” technology in photolithography.

Figure 4-2-1 The Lambda Physik LPX220i showing the control console and laser workstation.

Figure 4-2-2 Laser delivering system and sample stage of the laser workstation shown in Fig. 4-2-1.

4.3 Sputtering System

The sputtering system is an Applied Materials Endura PVD. It has four sputtering chambers and two transfer chambers (i.e. buffer-transfer chamber and high vacuum transfer chamber). The buffer-transfer chamber is used to receive and deliver back wafers to two cassette loadlocks whereas the later one is used to receive wafers from the pre-clean chamber and transfers them to the sputter chambers. Fig. 4-3-1 shows the schematic representation of the sputtering system. The sputtering chamber uses circular planar magnetron sources with DC capability. The Co deposition uses 800 watts of DC power and the process pressure is around 4 mTorr.

Figure 4-3-1 Schematic representation of the sputtering system.

Sputtering system

In the DC magnetron sputtering process, argon gas is used to create glow discharge in which free electron is created through ionization. The magnetron source is used to confine the electrons near the target surface. With the increase of electrons, it promotes the ionizing collisions. To sustain the dc discharge, cathode in the system is used to emit secondary electrons when struck by ions. When the target surface is bombarded by atoms, ions or molecules, the sputtered atoms are ejected into the gas phase depending on the kinetic energy of the impinging particles. Eventually, the sputtered atoms deposited upon the substrates to form the specified thin film. The use of magnetron source causes the current densities at the target to be increased and this has allowed the glow discharge to be sustained at much lower pressures. Having such a low pressure, most of the sputtered atoms in magnetron sources arrive at the wafer without undergoing any collisions with the sputter-gas atoms. Therefore, utilizing this method of sputtering can enhance the sputter yield for the sample.

4.4 Characterization Techniques

To characterize and evaluate the as-deposited and laser-annealed samples, the XRD, micro-Raman spectroscopy, four-point probe, SEM, TEM, and AFM technique were used.

Four-point probe

The purpose of the four-point probe technique is to measure the resistivity of semiconductor material. It can measure either bulk or thin film samples. A CPS Probe Station was used for the sample characterization. The system consists of four equally spaced tungsten metal tips with a finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. A high impedance current source is used to supply current through the outer two probes whereas the voltage across the inner two probes was measured using a voltmeter (see Fig. 4-3-1). Hence, for a very thin layer (thickness $t \ll s$), the sheet resistance

$$R_s = \rho/t \quad (4.1)$$

can be governed by

$$R_s = 4.53 \left(\frac{V}{I} \right) \quad (4.2)$$

where ρ is the resistivity, t is the film thickness, V is the voltage measured between inner probes, and I is the current applied between the outer probes.

Figure 4-4-1 Schematic of a four-point probe technique.

X-ray diffraction

A Philips X’Pert X-Ray Diffraction (XRD) system was used to identify the thin film phases and crystalline structure of the laser-annealed samples. It is a four-axis diffractometer (with 2θ , ω , ϕ and ψ) made especially for materials analysis purposes. This system is equipped with parallel beam optics, which consists of primary optical path and secondary optical path, shown in Fig. 4-4-2. The corresponding components of each optical path are listed in Table 4-4-1.

The x-ray source is a ceramic filament tube with a Cu-target, giving out K_{α} of $1.54 \text{ \AA}$ and K_{β} of $1.39 \text{ \AA}$. The filament is made of tungsten operating at 40 kV and 45 mA. The x-ray mirror in the system eliminates the K_{β} radiation giving a monochromatic Cu K_{α} radiation.

Figure 4-4-2 The optical path of a Philips X'Pert XRD system [manual handbook].

Table 4-4-1 Components of the Philips X'Pert XRD system shown in Fig. 4-4-2.

Primary Optical Path	Secondary Optical Path
1. X-ray tube	7. Sample
2. Focal point of x-ray tube	8. Parallel beam collimator
3. Beta filter	9. Fixed receiving slit
4. Soller slit	10. Flat crystal monochromator
5. Fixed divergence slit	11. Detector
6. Mask	

A calibration was first carried out prior to the thin film scan of the samples. The calibration was started by first carrying out a manual scan, so that an optimum elevation position of the stage can be found. Then, a thin film scan was performed in 2θ scanning mode while an incidence grazing angle of 1° was used. The 2θ range was chosen from 20° to 80° with a step size of 0.04° in a step interval of 2 seconds. Besides, 2θ - Ω scan was carried out the bulk study.

Auger electron spectroscopy

Auger electron spectroscopy (AES) can be used to study the depth profile and atomic concentration of materials. It identifies elemental compositions of surfaces by measuring the energies of the emitted Auger electrons. The AES technique is a surface sensitive analysis tool. Auger

electrons that escape from deeper in the sample may contribute loss tails to the spectrum background due to the secondary and backscattered electrons. The sum of these interfering signals is much greater than the Auger signals themselves as they have broad energy distributions that tail into the Auger region. Although Auger electrons fail to emerge with their characteristic energies from a deep layer, a differentiation adopted by the Auger display algorithms can enhance the signal relative to the interferences.

A PHI SMART-200 Auger system was used in the experiments in order to study the depth profile and atomic concentration of the as-deposited and laser-annealed samples. The system is equipped with an ion-gun setting operating at 2 keV and 700 nA. The ion source that is used to raster the sample is Ar^+ and the raster size is $2 \times 2 \text{ mm}^2$. The sputter etch rate based on SiO_2 is $\sim 98 \text{ \AA/min}$. The electron gun was operated at 20 keV, 10 nA, and with the gun tilted at 30° . The detection limit of the system is around 0.1 to 1 atomic percentage, and it has the surface sensitivity of top 50 $\text{\AA}$.

Scanning electron microscopy

Scanning electron microscopy (SEM) provides topographical information at magnifications of 10X to 100,000X with virtually unlimited depth of field. The sample is scanned with a focused beam of electrons which produce secondary electrons as the incident beam irradiates on the specimen. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen. In the experiment, a PHILIPS FEG SEM XL30s operating at 5 kV was utilized to characterize the surface topography.

Transmission electron microscopy

A 200 kV of Philip Transmission Electron Microscopy (TEM) system was used for high-resolution observation of the interior structure of the samples. The system which was used to study the cross-sectional microstructures are FEI CM200 FEG TEM with Gatan GIF/PEELS. In the TEM, the samples are examined by passing the electron beam through them, revealing more information of the internal structure of specimens. Hence, prior the exposure to the electron beam, the samples must be milled. In conjunction with the TEM analysis, the energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) analysis were carried out in order to investigate elemental composition and elemental analysis, respectively.

Electron energy loss spectroscopy

An Electron energy loss spectroscopy (EELS) technique is used to investigate the elemental and chemical information in samples. The EELS involves the bombardment of a sample with a monoenergetic beam of electrons. The technique is frequently used in association with TEM. The electrons impinging on the sample may lose energy by a variety of mechanisms. Hence, the elemental composition and atomic bonding state can be determined by analyzing the energy with the spectroscope attached under the electron microscope. In the experiments, the FEI CM200 FEG TEM with Gatan GIF/PEELS was used to implement the EELS analysis.

Electron dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDX) is an elemental analysis technique performed in conjunction with SEM or TEM. It utilizes x-rays that are emitted from the sample during bombardment by the incident electron beam

to characterize the elemental composition of the analyzed volume. The EDX detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted.

Atomic force microscopy

Atomic force microscopy (AFM) was used to monitor the surface profiles and roughness of the laser-annealed samples. The AFM uses a physical probe raster scanning across the sample using piezoelectric ceramics. A feedback loop is used to maintain a constant interaction between the probe and the sample. The position of the probe and the feedback signal are electronically recorded to produce a three dimensional map of the surface or other information depending on the specialty probe used. The data output is either a three dimensional image of the surface or a line profile with height measurements. Furthermore, the surface roughness parameters such as RMS (root mean square) can be obtained for the output data. In the experiments, the Digital Instruments was used to carry out the surface morphology study.

4.5 Summary

In this project, 7 types of samples were prepared in order to study the laser-induced silicidation on n-type Si substrate. The samples are listed as below.

1. Ti (12.5 nm)/Co (12 nm)/Si
2. Ti (12.5 nm)/Co (13 nm)/Si
3. Ti (12.5 nm)/Co (13 nm)/PAI (50 nm)/Si
4. TiN (20 nm)/Co (13 nm)/Si
5. TiN (20 nm)/Co (13 nm)/PAI (50 nm)/Si

6. Co (13 nm)/Si
7. Co (8 nm)/Si

Device structures such as diode and Kelvin test structures were selected for electrical performance study.

To characterize and evaluate the as-deposited and laser-annealed samples, XRD, four-point probe, SEM, TEM, and AFM technique were used.

Chapter 5 Simulation of Laser Interactions with Materials

5.1 Introduction

The irradiation of pulsed laser on samples can be simulated using the SLIM (Simulation of Laser Interactions with Materials) software. This software can be used to simulate heating, melting and ablating of pulsed-laser irradiated materials. It incorporates temperature and phase-dependent thermophysical and optical properties of the material and allows the simulation of propagating liquid and vapour interfaces. It also allows incorporation of any type of user defined laser pulse shape. Besides, simulation of laser interaction with multi-layered structures, subject to a maximum of three layers, can be implemented too. The simulation software creates data output in a graphical format. Only single pulsed-laser irradiation can be simulated with a temperature distribution profile.

The SLIM software is fundamentally developed based on a one-dimensional heat equation. The one-dimensional heat equation that governs the non-uniform temperature distribution in the substrate is a function of the depth z and time t (equation 3.5 in Chapter 3).

5.2 Simulation of Single-pulsed Laser Annealing

In order to carry out the simulation, the thermophysical and optical properties of the material must be provided. The thermophysical properties includes the melting temperature, boiling temperature, density, latent heat of melting, latent heat of vaporization, thermal conductivity, and volume heat capacity of the material of interest. The optical properties required are the

Chapter 5 Simulation of Laser Interactions with Materials

absorption coefficient and reflectivity of material. The thermophysical and optical properties of Si, amorphous Si, Co, Ti, and TiN are listed in Table 5-1-1.

Table 5-1-1 The thermophysical and optical property of materials [60, 63, 71, 72, 73, 74].

Parameters	Si	α -Si	Co	Ti	TiN
Melting point (K)	1685	1420	1768	1941	3203
Boiling point (K)	3173	3538	3200	3560	3563
Density (g/cm ³)	2.33	-	8.8	4.54	4.5
Latent heat of melting (J/cm ³)	3844	3076	2314	1997	3700
Latent heat of vaporization (J/cm ³)	31921	-	57112	44628	48208
Thermal conductivity at 25°C (W/cm-K)	1.412 (solid) 4.3 (liquid)	-	0.96		0.19
Specific heat mass at 25°C (J/g-K)	0.7	-	0.4573	0.5202	0.60
Thermal diffusivity (cm ² /s)	0.9	-	0.06	0.1	0.07
Thermal conductivity (W/cm K) -solid phase	$1.9e03x^{-1.26}$	0.018	$-8e-10x^3 + 3e-06x^2 - 2.9e-03x + 1.67$	$-1.86e-01x^{0.3042} - 1.86e-01x^{0.3042} + 1.09e-01(x + 8.35e-03)^{0.4377} + 1.001$	$5e-11x^3 + 3e-07x^2 - 0.0009x + 0.5717$
-liquid phase	0.7	4.3	0.431	0.17	0.283

Volume heat capacity (J/cm ³ K) - solid phase	$1.07\text{e-}09x^3 - 3.06\text{e-}06x^2 + 3.1\text{e-}03x + 0.98$	$2.64\text{e-}04x - 3.82\text{e}04x^{-2} + 2.06$	$-2.86\text{e-}09x^3 + 8.42\text{e-}06x^2 - 3.64\text{e-}03x + 4.35$	$-1.59\text{e-}02x^{0.5103} - 3.26\text{e-}02x^{0.5274} + 6.7\text{e-}03(x + 4.41\text{e-}03)^{0.798} + 1.664$	$1\text{e-}09x^3 - 5\text{e-}06x^2 + 0.0068x + 1.7468$
- liquid phase	2.42	2.49	5.19	3.18	3.34
Coefficient of linear thermal expansion (10 ⁻⁶ per °C)	2.6	-	12.5	8.9	9.35
Absorption coefficient (cm ⁻¹) at 248 nm	1.81e06	1.4e06	9.27e05	6.13e05	7.8e05
Reflectivity at 248 nm	0.66	0.55	0.40	0.235	0.35

where x is the temperature.

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A tri-layered structure was chosen to simulate the laser interaction with cap/Co/Si system while a bi-layered structure was used to simulate the laser interaction for Co/Si system without capping layer. A square pulse with a pulse duration of 23 ns was selected. Subsequently, the temperature distribution profiles for laser fluences of 0.2 to 0.5 J/cm² are extracted from the simulation. On top of that, the interaction of laser with silicon and amorphous silicon were also simulated in order to supplement the understanding of laser-annealed capped Co/Si system with and without PAI layer. With these data, a rough estimation of the laser interaction with the metal can be studied.

Some assumptions are made in order to facilitate the simulation of temperature profiles.

1. The pre-annealed materials are assumed to be uniform distributed.
2. The laser beam area is assumed to be 2.5 mm × 2.5 mm and the heat is propagated downward (along the z-axis) with an infinite thick of heat sink (i.e., silicon substrate).
3. An overestimated temperature profiles may have achieved as a square shape of laser pulse was assumed during the simulation. This is because the laser beam is a rectangular Gaussian profile practically, which has been discussed in Sec. 3.1.1.
4. The TiO_x and CoO_x layer on the surface of the as-deposited samples is neglected for the simulated structures since it is very thin (3 to 5 nm).

5.3 Results of Simulation

Crystalline and amorphous silicon

Figure 5-3-1 displays the melt depth of crystalline and amorphous silicon for laser fluences in the range of 0.1 to 1 J/cm². The melt depth was first simulated by inputting the thermophysical and optical properties of the materials from Table 5-1-1 into the SLIM simulation program. Then, different melt depth profiles were simulated by varying the laser fluence. It shows that with the fluence of 0.5 J/cm², the crystalline silicon starts to melt whereas the amorphous silicon starts to melt at a lower fluence of 0.4 J/cm². As the fluence increases, the melt depth increases proportionally for both types of silicon. These threshold fluences for melting shown by the simulation results for crystalline and amorphous silicon have been empirically confirmed [75].

Figure 5-3-1 Melt depth of crystalline and amorphous silicon for the fluence range of 0.1 to 1 J/cm².

Ti/Co/Si, TiN/Co/Si and Co/Si system

The temperature profiles of Ti (12.5 nm)/Co (13 nm)/Si, TiN (20 nm)/Co (13 nm)/Si, and Co (13 nm)/Si sample for 0.2, 0.3, 0.4 and 0.5 J/cm² are shown in Figs. 5-3-2, 5-3-3, and 5-3-4, respectively. Boundary lines drawn in dash pattern are used to indicate different layers of the samples. The temperature distribution profiles illustrate that the temperature decreases gradually as the heat propagates towards the substrate.

It can be observed from the three figures that the surface temperature increases proportionally with increasing laser fluence. The temperature distribution of the interface for Ti/Co, TiN/Co and Co/Si can be clearly observed. Among the metal surfaces, TiN has higher temperature distribution profiles compared to Ti and Co. This is attributed to high optical absorption coefficient of TiN at 248 nm under the UV light irradiation.

Figure 5-3-2 Temperature distribution profile of a Ti/Co/Si system for 0.2 to 0.5 J/cm².

Figure 5-3-3 Temperature distribution profile of a TiN/Co/Si system for 0.2 to 0.5 J/cm².

Figure 5-3-4 Temperature distribution profile of a Co/Si system for 0.2 to 0.5 J/cm².

5.4 Summary

The thermophysical and optical properties of materials were investigated and provided for the SLIM simulation. The SLIM was used to

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give a preliminary understanding of temperature distribution profiles during the pulsed-laser annealing. From the temperature distribution profiles, the maximum surface temperature and interface temperature of the film stacks can be investigated. The simulation results show that the surface temperature increases with the increasing of laser fluence. Among the simulated film stacks, TiN-capped Co/Si system experiences the highest surface temperature distribution. This is because of its high optical coupling at 248 nm of light.

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6.1 Study of Single-pulsed Laser Annealing

6.1.1 Preliminary study of Ti/Co/Si system

A preliminary study of laser induced silicidation using single pulse annealing on Ti (12.5 nm)/Co (12 nm)/Si without PAI (pre-amorphization implantation) layer was carried out.

Experimental

A 12 nm Co layer was deposited, followed by the deposition of a 12.5 nm Ti layer using DC magnetron sputtering without breaking the vacuum. The Ti cap is supposed to protect the Co during laser annealing as Co is vulnerable to oxygen. The samples were then irradiated with a 248 nm KrF laser. Only one pulse of laser with a pulse duration of 23 ns at 0.6 J/cm^2 was used.

Phase Analysis

Figure 6-1-1 shows the thin film scan (with incident angle of 1°) XRD spectra of Ti/Co on Si (100) after a single-pulsed laser annealing at 0.6 J/cm^2 . As compared to a RTA-annealed sample, a diffraction peak at 28.9° corresponding to CoSi_2 (111) phase can be identified. MicroRaman spectra (not shown here) confirm that there are no frequency shifts at 204, 220, and 150 cm^{-1} for the pulsed-laser annealed samples [76] indicating the absence of CoSi and Co_2Si phases. In addition, no frequency shifts located at 305 and 325 cm^{-1} are observed too, further implying the absence of CoSi and CoSi_2 [77].

Figure 6-1-1 Grazing incidence XRD spectra of a Ti/Co/Si system without PAI after a single-pulsed LTA at 0.6 J/cm^2 . A RTA-annealed sample is included for comparison. The RTA experiments were performed using a 2-steps RTA at 450°C and 825°C for 30 seconds in a N_2 ambient.

Depth Profile Analysis

Figure 6-1-2 shows the AES depth profiles of a Ti/Co/Si sample before and after a 0.6 J/cm^2 laser annealing. It can be seen that a TiO_x layer remains intact on the surface of the Ti/Co/Si sample before and after annealing. The rapid heating by the single-pulsed laser annealing has very little effect on the depth profile of TiO_x , implying insignificant diffusion of oxygen atoms during the laser annealing process. On the other hand, the Ti atoms beneath the TiO_x layer have diffused towards the Si substrate and intermixed with Co and Si, leading to the formation of CoTi silicide.

Figure 6-1-2 AES depth profiles of a Ti/Co/Si system without PAI (a) before annealing and (b) after annealing with a single laser pulse at 0.6 J/cm^2 .

Microstructure Analysis

Figure 6-1-3 shows the cross-sectional TEM obtained from the Ti/Co/Si sample of which the XRD spectra has been shown in Fig. 6-1-1. The top layer of $\sim 5 \text{ nm}$ is an amorphous TiO_x . The middle layer of $\sim 72 \text{ nm}$ is an amorphous CoTi silicide (i.e., α -CoTi silicide) with a uniform surface and the bottom layer ($\sim 23 \text{ nm}$) is a CoTi silicide that is highly orientated to the (111) direction of the Si substrate. The EDS and Auger analysis of the amorphous CoTi silicide layer

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shows that the ratio of Co:Ti:Si near the surface and immediately above the textured layer is 23:40:37 and 33:12:55, respectively. Whereas, the ratio of Co:Ti:Si in the textured CoTi silicide layer is about 14:4:82. Figure 6-1-3(b) shows a HRTEM image of the highly textured (111)CoTi silicide/(111)Si system on the (100) Si substrate. The favorable growth of the CoTi silicide along the (111) plane is due to its lowest interface energy with the (111) Si plane [78]. Crystalline defects resembled branches and stems appearing as dark contrast correspond to Co-rich region (relative to Ti) revealed by the EELS Co elemental mapping as shown in Fig. 6-1-4. Table 6-1-1 illustrates the comparison of the estimated the thickness for each layer obtained from XTEM and AES shown in Fig. 6-1-3(a) and Fig. 6-1-2(b), respectively.

Figure 6-1-3 (a) XTEM image and (b) HRTEM image of the Ti/Co/Si sample after single-pulsed laser irradiation at 0.6 J/cm².

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Table 6-1-1 Comparison of thickness obtained from XTEM and AES for the Ti/Co/Si system without PAI after single-pulsed laser annealing at 0.6 J/cm².

XTEM		AES	
Layer	Estimated thickness (nm)	Sputtering time (minute)	Estimated thickness (nm)
TiO _x	5	0 to 0.5	5
α-CoTi silicide	72		
Highly textured CoTi silicide	23		
Total silicide thickness (excludes TiO _x)	95	0.5 to 10	95

The possible growth mechanism for the formation of the microstructure in Fig. 6-1-3 is as follows. When a single pulse laser of 0.6 J/cm² is irradiated on the surface of a Ti/Co/Si stack, the energy of the laser pulse is high enough to cause melting of Ti, Co and Si. As it can be seen from Fig. 6-1-3, the melt front has propagated down to ~100 nm of depth. In the initial molten state, the Ti/Co metal layers and the Si substrate undergo a mixing via liquid phase diffusion. As a result, a variation in the composition of the Co and Ti was resulted in the liquid phase. When the melt front reaches the substrate during the laser irradiation, the single crystalline Si substrate which acts as a seed for the epitaxial regrowth, facilitates the nucleation in an epitaxial manner during solidification. The growth kinetic is based upon liquid-phase epitaxy regrowth [42, 79]. The rapid quenching rate of the melt has resulted a large amount of supercooling, and this gives rise to a driving force for a solidification accompanied by a decrease in the free energy of the system. During the solidification, the (111) plane of the CoTi silicide tends to grow along the (111) Si substrate due to its lowest interface energy.

Figure 6-1-4 (a) EELS elemental mapping of Co of a section of the highly textured CoTi silicide layer. (b) The corresponding XTEM micrograph of (a).

As the solidification front proceeds further into the molten liquid, due to the presence of a high concentration of Ti impurity ($\sim 12\%$ as shown in Figs. 6-1-2(b) and 6-1-3(a)), a change in the thermodynamics has possibly led to a transition from the textured CoTi silicide to an amorphous CoTi silicide similar to the phenomenon suggested by Gong *et al.* [80] for the solidification transition from a crystalline to an amorphous phase. The presence of Ti atoms has modified the solidification temperature and growth dynamics [11]. This is possible since there is a large negative heat of mixing associated with the presence of a large quantity of the Ti impurities in the composition range as detected by the Auger and EDS analysis data shown in Fig. 6-1-2(b) and Fig. 6-1-3(a), respectively. The formation of the amorphous CoTi silicide can also be resulted from the supercooled/undercooled liquid in which its temperature has fallen below the melting temperature of the CoTi silicide amorphous phase [81, 82]. As a result of the supercooled liquid, the velocity of the solidifying interface has exceeded the estimated value of 1.5 m/s [42]. With this fast

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solidification velocity, the amorphous CoTi silicide layer propagates upwards until it reaches the surface.

Figure 6-1-5 shows the TEM plane view of a pulsed-laser annealed Ti/Co/Si stack. Cellular structures which are typical consequences of constitutional supercooling (CSC) [34, 35] can be seen. The presence of the CSC phenomenon is because the actual temperature in the CoTi silicide liquid near to the solid-liquid interface is less than that of the liquidus temperature. In addition, due to the presence of a compositional gradient of solute atoms (i.e. Co and Ti) as a function of depth in the melt, CSC takes place along with the segregation of solute atoms during the solidification. Since the solubility of the Co and Ti atoms in the solid Si is much less than that in the liquid Si, the solute atoms are rejected from the solid during the solidification in the supercooled liquid ahead of the interface. This results in a lower Co concentration detected in the textured CoTi silicide than that near the interface of the amorphous CoTi silicide and the highly textured CoTi silicide (Fig. 6-1-3(a)). In addition, there is an obvious increment in the Co concentration between the 7.5 and 10 minutes of the sputtering time in Fig. 6-1-2(b). Comparing to the Co elemental mapping in Fig. 6-1-4, the dark contrasts shown by the textured layer in the HRTEM lattice image in Fig. 6-1-3(b), which resemble branches and stems extending upwards in the (100) and outwards in the (111) direction are Co-rich CoTi silicide. The presence of the segregation of solute atoms has contributed to the growth of the defect-occupied CoTi silicide grains during the solidification, and this supports the CSC phenomenon.

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Figure 6-1-5 Plane view TEM of a Ti/Co/Si sample after annealing at 0.6 J/cm².

A schematic of the textured CoTi silicide with a high concentration of crystalline defects is illustrated in Fig. 6-1-6. A transitional layer of about ~3 nm (see Fig. 6-1-3(b)) is suspected to be the mechanism responsible for the “milky” contrast seen in the plane view TEM in Fig. 6-1-5.

Figure 6-1-6 Schematic of the textured CoTi silicide showing defects due to segregation of Co impurities during CSC.

6.1.2 In-depth study of Ti/Co/Si system with & without PAI

Experimental

A 13 nm Co layer was deposited, followed by the deposition of a 12.5 nm Ti layer using DC magnetron sputtering without breaking vacuum on blanket Si substrate with and without 50 nm PAI layer. In this experiment, a single-pulsed laser in an energy range of 0.2 J/cm² to 0.7 J/cm² was implemented.

Phase Analysis

Figure 6-1-7 shows the grazing incidence XRD spectra of a Ti/Co/Si system without and with PAI, respectively, after a single-pulsed LTA with fluences of 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, and 0.7 J/cm². As can be seen from Fig. 6-1-7, a peak at 28.9° that corresponds to CoSi₂ in the (111) plane was detected for the fluences of 0.4, 0.5, 0.6 and 0.7 J/cm², whereas no peak can be detected for fluences below of 0.4 J/cm². The resultant phase may be in amorphous or partial amorphous since the full-width half-maximum of the XRD peaks is broad.

Figure 6-1-7 XRD spectra of a Ti/Co/Si system without PAI after a single-pulsed LTA for a fluence range of 0.2 to 0.7 J/cm².

For Ti/Co/Si with a 50 nm PAI layer, a peak at $\sim 28.8^\circ$ can be observed for laser fluence down to 0.2 J/cm², as can be seen in Fig. 6-1-8. 0.2 J/cm² is able to induce silicidation since a XRD peak corresponding to the (111) CoSi₂ was detected.

Figure 6-1-8 XRD spectra of a Ti/Co/Si system with PAI after a single-pulsed LTA for fluence range of 0.2 to 0.7 J/cm².

Depth Profiles Analysis

Figure 6-1-9 shows the atomic concentration distribution of the Ti/Co/Si system without PAI. Fig. 6-1-9(a) illustrates the depth profiles before annealing while Figs. 6-1-9(b) and (c) show the depth profiles after annealing at 0.2 and 0.3 J/cm², respectively. For the fluence at 0.2 J/cm², the Ti and Co atoms start to interdiffuse and diffuse into the Si substrate after the single-pulsed irradiation. For the fluence at 0.3 J/cm², CoTi silicide has been formed.

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Figure 6-1-9 AES of a Ti/Co/Si system without PAI (a) before annealing and after single-pulsed laser annealing at (b) 0.2 and (c) 0.3 J/cm².

(a)

(b)

Figure 6-1-10 AES of a Ti/Co/Si system with PAI after a single-pulsed LTA at (a) 0.2 and (b) 0.3 J/cm².

The depth profiles of a Ti/Co/Si system with PAI layer after a single-pulsed laser annealing at 0.2 and 0.3 J/cm² are shown in Figs. 6-1-10(a) and (b), respectively. Compared to the depth profile of the as-deposited sample in Fig. 6-1-9(a), the atomic distributions show an obvious change for 0.2 J/cm². The Si, Co, and Ti have interdiffused and intermixed with each other, which provide evidence that melting has occurred with the presence of the PAI layer (the microstructure will be discussed in a later part). Similar phenomenon can be observed for a single-pulsed of laser annealing at 0.3 J/cm² too. Si, Co, and Ti

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have interdiffused and intermixed in liquid phase and solidify to form CoTi silicide.

Microstructural Analysis

Two single-pulsed laser-annealed samples were selected for microstructural analysis using XTEM. Figure 6-1-11 shows the XTEM of the Ti/Co/Si system without PAI layer after a single-pulsed annealing at 0.2 J/cm^2 . The as-deposited sample is shown in inset and columnar grain structures are observed in the Ti/Co film stacks. After 0.2 J/cm^2 of LTA, it can be seen that the Ti and Co layer stay intact as the columnar grain structures can still be seen. Table 6-1-2 shows the thickness of the film stacks before and after annealing. The amorphous interlayer was excluded from the evaluation of the film thickness as discussed in Section 4.1.

Figure 6-1-11 XTEM of a Ti/Co/Si system without PAI after a single-pulsed laser annealing at 0.2 J/cm^2 . The inset shows the XTEM of an as-deposited sample.

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Table 6-1-2 Estimated thicknesses of film stacks obtained from the XTEM micrograph for the Ti/Co/Si system before and after annealing shown in Fig 6-1-11.

Layer	Before annealing (nm)	After annealing (nm)
Ti	12.5	10.2
Co	13	11.6

From table 6-1-3, a mild solid-state diffusion have occurred for Ti and Co at the interface. Therefore, interface diffusion have taken place. This can be confirmed by the AES shown in Fig. 6-1-9(b), where the Ti and Co distribution at the interface has propagated as compared to the as-deposited sample in Fig. 6-1-9(a).

From the XTEM micrograph in Fig. 6-1-11, the thickness of TiO_x has increased from ~ 3.5 nm to ~ 4.8 nm after LTA. This may be attributed to strong affinity to oxygen possessed by Ti [32]. Besides, its high reactive at high temperatures above 550°C may have caused it to interact with oxygen easily. From the SLIM simulation, the surface temperature of Ti/Co/Si has reached ~ 800 K for a laser fluence of 0.2 J/cm^2 . Hence, the Ti atoms in the film stacks near the TiO_x layer may have diffused and interacted with oxygen from the annealing ambient during LTA. From the XRD results shown in Fig. 6-1-7 and AES results shown in Fig. 6-1-9(b), a single-pulsed laser at 0.2 J/cm^2 does not result any silicidation. The laser energy density is just enough to cause diffusion at the interface of Ti/Co and Co/Si.

Figures 6-1-12(a) and (b) illustrate the XTEM and HRTEM of Ti/Co/Si with a 50 nm PAI layer after a single-pulsed LTA at 0.2 J/cm^2 , respectively. As can be seen from the XTEM micrographs, the top layer of ~ 5.3 nm is an amorphous TiO_x . The subsequent layer of ~ 28 nm is an amorphous CoTi silicide. The third layer is a coarse-grained polycrystalline CoTi silicide (i.e.,

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poly-CoTi silicide), with a thickness of ~ 21.3 nm. The bottom layer of ~ 16.7 nm is a textured Si which is full of defects oriented in the (111) direction. The EDX reveals that the atomic concentration ratio for the amorphous CoTi silicide and polycrystalline CoTi silicide are Co:Ti:Si $\sim 24.8:12.1:63.1$ and Co:Ti:Si $\sim 78.8:0.7:20.5$, respectively. No Co and Ti elements were detected by EDX for the textured Si layer. To further ascertain there is no distribution of Co in the textured Si, a thickness comparison between TEM and AES was carried out and the results are given in Table 6-1-3. From the AES depth profile shown in Fig. 6-1-10(a), the CoTi silicide thickness can be estimated from the range of 0.5 to 5.5 minute of the sputtering time as the tail of Co distribution ended at ~ 5.5 minute. The layer from 0 to 0.5 minute of the sputtering time is TiO_x , with a thickness of approximately 4.9 nm. Therefore, the silicide thickness is about 49 nm estimating from the AES data. The CoTi silicide analyzed from XTEM comprises the amorphous CoTi silicide and the polycrystalline CoTi silicide.

Figure 6-1-12 (a) XTEM and (b) HRTEM of a Ti/Co/Si system with PAI after a single-pulsed laser annealing at 0.2 J/cm^2 .

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Table 6-1-3 Comparison of thickness obtained from XTEM and AES for the Ti/Co/Si system with PAI after a single-pulsed annealing at 0.2 J/cm².

XTEM		AES	
Layer	Estimated thickness (nm)	Sputtering time (minute)	Estimated thickness (nm)
α -TiO _x	5.3	0 to 0.5	4.9
α -CoTi silicide	28		
Poly-CoTi silicide	21.3		
Total silicide thickness exclude TiO _x	49.3	0.5 to 5.5	49
Textured Si	16.7		

One possible growth mechanism of the poly-CoTi silicide and textured Si in Fig. 6-1-12(a) is explosive crystallization. When the single-pulsed laser of 0.2 J/cm² irradiates on the sample, the laser melts neither the Ti nor Co layer as it has been shown by the XTEM of a Ti/Co/Si system without PAI after a 0.2 J/cm² of LTA (see Fig. 6-1-11). Therefore, the 0.2 J/cm² laser energy may have melted only a thin Si amorphous layer at the top of the amorphous Si since it has lower melting temperature. The laser energy might have caused melting at a lower melting point of amorphous Si, i.e., below 1349 K for amorphous layer produced by ion implantation [83]. Besides, the latent heat of fusion is less for amorphous Si than for single crystal Si [84]. Subsequently, the liquid phase of Si may have favored the diffusion of Ti and Co atoms, and caused the melting of the Co/Ti film stacks since the solute atoms are more favorable stay in liquid rather than in solid phase.

As this compound liquid begins to solidify, the latent heat released from the liquid has caused the solid phase epitaxy regrowth for the remaining of amorphous Si without further diffusion of Co into this regrowth amorphous Si. Subsequently, the solid phase epitaxy regrowth of the amorphous Si from the amorphous/crystal Si interface has facilitated a further growth of grains in the

polycrystalline CoTi silicide, giving rise to a coarse-grained polycrystalline CoTi silicide. The occurrence of explosive crystallization can be attributed to the difference in the thermal conductivity between the amorphous Si and crystalline Si [52, 68, 85]. Despite this resolidified textured Si is almost similar to the highly textured CoTi silicide layer seen in Fig. 6-1-3 with the defects orientate in the (111) plane, the chance of having CSC to occur during solidification is very small. This is because CSC only occurs at high laser energy density [7]. In addition, the interface between the textured Si and the Si substrate is smoother (see Fig. 6-1-12(b)) than the interface between the textured CoTi silicide and the Si substrate (see example in Fig. 6-1-3(b)). This imply that there is no segregation of solute atoms (i.e. Ti or Co) in this textured layer. The growth of this crystalline Si, which is full of defects in (111) plane, can be attributed to the solid phase epitaxy regrowth facilitated by the substrate in which it has acted as a template. As the solidification front proceeds toward the surface, a transition from the growth of polycrystalline CoTi silicide to the formation of amorphous CoTi silicide takes place. This transition of growth mechanisms is due to the high Ti distribution or supercooled liquid, which has been discussed in Section 6.1.1.

Figure 6-1-13(a) shows the XTEM micrograph of a Ti/Co/Si system without PAI after going through 0.3 J/cm^2 of single-pulsed LTA while Fig. 6-1-13(b) shows the high magnification of Fig. 6-1-13(a) along with the elemental results obtained from an EDX analysis. Three layers can be identified from XTEM. The top layer is TiO_x and the middle layer is amorphous CoTi silicide with the Co:Ti:Si ratio of 31:6:63. The bottom layer is polycrystalline CoTi silicide with the Co:Ti:Si ratio of 3:0.2:96.8. Table 6-1-4 illustrates the

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comparison of the thickness for each layer obtained from XTEM (Fig. 6-1-13(b)) and AES (Fig. 6-1-9(b)).

Figure 6-1-13 (a) Low magnification and (b) high magnification of XTEM for a Ti/Co/Si system without PAI after a single-pulsed laser annealing at 0.3 J/cm².

Table 6-1-4 Comparison of thickness obtained from XTEM and AES for the Ti/Co/Si system without PAI after a single-pulsed annealing at 0.3 J/cm².

XTEM		AES	
Layer	Estimated thickness (nm)	Sputtering time (minute)	Estimated thickness (nm)
Amorphous TiO _x	5.7	0 to 0.5	4.5
α-CoTi silicide	29.5		
Poly-CoTi silicide	21.9		
Total silicide thickness (excludes TiO _x)	51.4	0.5 to 6.6	54.9

Figure 6-1-14 shows the XTEM micrograph of a Ti/Co/Si system with a PAI layer after going through 0.3 J/cm² of single-pulsed LTA. Similarly, a three-layered structure can be identified from XTEM. The top layer is TiO_x and the middle layer is amorphous CoTi silicide with the Co:Ti:Si ratio of 33:12:55. The bottom layer is polycrystalline CoTi silicide with the Co:Ti:Si ratio of 32.3:0.7:67. Table 6-1-5 tabulates the comparison of the thickness for each layer obtained from XTEM (Fig. 6-1-14(a)) and AES (Fig. 6-1-10(b)).

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Figure 6-1-14 (a) XTEM and (b) HRTEM of a Ti/Co/Si system with a PAI layer after a single-pulsed laser annealing at 0.3 J/cm².

Table 6-1-5 Comparison of thickness obtained from XTEM and AES for the Ti/Co/Si system with PAI after single-pulsed annealing at 0.3 J/cm².

XTEM		AES	
Layer	Estimated thickness (nm)	Sputtering time (minute)	Estimated thickness (nm)
α-TiO _x	6	0 to 0.5	4.5
α-CoTi silicide	38.9		
Poly-CoTi silicide	20		
Total silicide thickness (excludes TiO _x)	58.9	0.5 to 6.6	54.9

A single-pulsed laser annealing at 0.3 J/cm² has resulted in almost the same thickness of polycrystalline silicide for the Ti/Co/Si system with and without PAI (see Fig. 6-1-13 and 6-1-14). The microstructures of the silicide formed for the samples with and without PAI are almost similar too. Both of them consist of amorphous CoTi silicide and polycrystalline CoTi silicide. Besides that, the interface between the silicide and Si substrate is smooth, and no CSC phenomenon is observed. Nevertheless, based on the TEM results shown in Fig. 6-1-13(a), a lower density of polycrystalline CoTi silicide is

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found for the samples without PAI compared to the samples with PAI. Henceforth, the lower density of polycrystalline CoTi silicide might have caused the difficulty in detecting Co silicide XRD peak for sample without PAI (Fig. 6-1-7). For the sample with PAI layer, there is no remaining PAI layer being observed. Therefore, the melt front is predicted to have reached the interface of amorphous Si/Si during irradiation.

For both PAI and non-PAI sample, the formation of the amorphous CoTi silicide is due to a high Ti distribution in liquid phase during rapid solidification, and this has been discussed in a previous section.

Sheet Resistance

The morphological stability was investigated by measuring the sheet resistance of the laser-annealed silicides and is plotted in Figure 6-1-15. The sheet resistance is inversely proportional to film thickness, i.e., $R_s = \rho/t$, where ρ is the material resistivity. The PAI and non-PAI case have the same trend of sheet resistance profiles: they have high value at low fluence initially, then they reduces when higher fluences were used and eventually saturate at high fluence at about $38 \Omega/\square$. However, the samples with PAI show a lower sheet resistance on the average than that of the samples without PAI. This is because thicker CoTi silicide has been formed for the PAI samples and was confirmed by the XTEM shown in Figs. 6-1-13 and 6-1-14 (see Tables 6-1-4 and 6-1-5, respectively).

For Ti/Co/Si without PAI, the sheet resistance is first shown to be very low, i.e. $\sim 17 \Omega/\square$, which is equivalent to the sheet resistance of the as-deposited film stacks of about $12 \Omega/\square$. When the laser fluence increases to 0.25 J/cm^2 ,

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the sheet resistance increases tremendously. As can be seen from Fig. 6-1-11, for 0.2 J/cm^2 , the films stack still stays intact whereas 0.3 J/cm^2 of fluence has melted the film stacks. These can be confirmed by the AES results shown in Figs. 6-1-9(b) and (c), and the XRD results (Fig. 6-1-7). The increase in the sheet resistance for 0.2 to 0.25 J/cm^2 can be attributed to the variation in electron scattering. The as-deposited film stacks which are grown by PVD (physical vapor deposition) method exhibits a limited atomic mobility [67, 86]. During the rapid heating, the thermal vibrations from the laser energy causes the Ti and Co atoms to be dislodged from the lattice alignment, and this subsequently affects the periodicity of the lattice. As a result, an incoherent scattering of the electron waves has occurred, which can be reflected by a drastic increase of the sheet resistance. Hence, more electrons scattering has been resulted when a higher fluence of 0.25 J/cm^2 is irradiated on the sample. There is no XRD peak if Co silicide was detected for 0.2 and 0.25 J/cm^2 , indicating that melting has not occurred. Instead, interface diffusion of Ti, Co and Si atoms has taken place for 0.2 J/cm^2 as can be seen from Fig. 6-1-9(b). When the fluence increases from 0.25 to 0.7 J/cm^2 , the sheet resistance decreases due to the formation of thicker amorphous and polycrystalline CoTi silicide. For the PAI case, the melting of the bi-layered film stacks (i.e., Ti/Co) and Si substrate has been observed starting from 0.2 J/cm^2 (Fig. 6-1-12).

Figure 6-1-15 Sheet resistance for single-pulsed laser-annealed sample with and without PAI in a range of fluence of 0.2 to 0.7 J/cm².

6.2 Study of Multiple-pulsed Laser Annealing

Experimental

In this part of work, the Ti (12.5 nm)/Co (13 nm)/Si system with and without a 50 nm PAI layer was used to study multiple pulsed laser annealing. The number of pulses, which was adopted in these experiments is 3, 5, 7, 10, 20, 50, and 100 pulses. As can be understood from the single pulsed-laser silicidation in Section 6.1, the fluence of 0.2 J/cm² does not cause any melting of the film stacks and Si for the non-PAI sample. By utilizing the mechanisms of non-melt, the silicide can be formed without jeopardizing a thick silicide since the melt depth has been shown to be an important factor in determining the silicide thickness. Besides that, a fully crystallized layer might be achieved after multiple-pulsed annealing based on the knowledge learnt from the

formation of amorphous CoTi silicide for single pulsed LTA [6, 79]. Therefore, multiple pulses of laser fluences at 0.2, 0.25, and 0.3 J/cm² were investigated in order to achieve the purpose of growing a thin silicide.

Phase Analysis

Figures 6-2-1(a) and (b) show the XRD spectra of a Ti/Co/Si system without PAI after multiple-pulsed laser annealing at 0.2 J/cm² and 0.3 J/cm², respectively. No obvious XRD peak was detected regardless the number of pulses used (including 50 and 100 pulses in which their XRD spectra are not shown in here). This further confirmed that no CoSi, Co₂Si or CoSi₂ was formed.

Figures 6-2-2(a) and (b) show the XRD spectra of a Ti/Co/Si system with PAI after multiple-pulsed laser annealing at 0.2 and 0.3 J/cm², respectively. For 0.2 J/cm², a XRD peak at ~28.8° which corresponds to (111) CoSi₂ is identified for less than 50 pulses of LTA. The XRD intensity becomes very weak for the 50-pulsed sample. Similar results can be identified for 0.3 J/cm². However, when the number of laser pulses increases to 10 and higher, the XRD peak at ~28.8° corresponding to CoSi₂ (111) vanishes. This is believed that a thicker amorphous CoTi phase has formed which can be proven using TEM (shown in later page).

Figure 6-2-1 XRD spectra of a Ti/Co/Si system without PAI after multiple-pulsed laser annealing at (a) 0.2 and (b) 0.3 J/cm².

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Figure 6-2-2 XRD spectra of a Ti/Co/Si system with PAI after multiple-pulsed laser annealing at (a) 0.2 and (b) 0.3 J/cm².

Depth Profile Analysis

In order to see the impact of multiple-pulsed laser annealing on Ti/Co/Si samples, AES depth profile analysis was carried out. Figures 6-2-3(a) and (b)

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show the atomic distribution of Ti/Co/Si system without PAI after 10 pulses of laser annealing at 0.2 J/cm^2 and 0.3 J/cm^2 , respectively. The depth profile of the as-deposited sample before annealing is shown in Fig. 6-1-9(a). It can be seen that Ti and Co have interdiffused and intermixed with Si for both 0.2 and 0.3 J/cm^2 . Melting of film stacks or/and substrate might have occurred during the subsequent pulses of LTA. This is possible since the reflectivity of Ti/Co on Si substrate decreases when the surface temperature increases (i.e., when the fluence increases) [50]. With the decrease in the reflectivity, the heat absorption would be enhanced. Hence, it is possible to cause the films stack to melt at higher number of pulses.

Figs. 6-2-4(a) and (b) show the AES depth profiles of a Ti/Co/Si system with PAI after 10 pulses of laser annealing at 0.2 J/cm^2 and 0.3 J/cm^2 , respectively. For the PAI case, since the study of single-pulsed laser annealing on the same system has already shown that 0.2 J/cm^2 is capable to form silicide by melting the Ti, Co and Si, hence the depth profiles obtained from Fig. 6-2-4 are contributed to the melting of bi-layered film stacks and the Si substrate. Such kind of atomic interdiffusion can only occur in the liquid phase in a short period of time since the diffusion coefficient of atom in liquids is high ($10^{-5} - 10^{-4} \text{ cm}^2\text{s}^{-1}$) [78]. This kind of interdiffusion is non-achievable in solid-state diffusion.

Comparing the atomic concentration of Fig. 6-2-3 with Fig. 6-2-4, the samples with the PAI layer has enhanced the diffusion of Si and Si has reacted with Co subsequently. Furthermore, nearly the same melt depths are obtained for PAI and non-PAI case for 10 pulses at 0.2 J/cm^2 and 0.3 J/cm^2 .

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Figure 6-2-3 AES of a Ti/Co/Si system without PAI after 10 pulses of laser annealing at (a) 0.2 and (b) 0.3 J/cm².

Figure 6-2-4 AES of a Ti/Co/Si system with PAI after 10 pulses of laser annealing at (a) 0.2 and (b) 0.3 J/cm².

Microstructure Analysis

Figure 6-2-5 shows the XTEM micrograph of the Ti/Co/Si without PAI layer after 20 pulses of laser annealing at 0.2 J/cm². Three layers can be identified, i.e. amorphous TiO_x, amorphous CoTi silicide and polycrystalline CoTi silicide. Based on the TEM analysis, the amorphous CoTi and polycrystalline CoTi silicide have the thickness of ~25 nm and 9.5 nm, respectively. Hence, the total silicide thickness is ~34.7 nm.

Figures 6-2-6(a) and (b) show the XTEM micrograph and HRTEM of the Ti/Co/Si sample with PAI after 20 pulses of laser annealing at 0.2 J/cm².

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From the XTEM micrograph shown in Fig. 6-2-6(a), the solidified layer comprises a ~ 11.5 nm layer of amorphous TiO_x , a ~ 52.6 nm layer of amorphous CoTi silicide, and a ~ 16 nm of polycrystalline CoTi silicide. Hence, the silicide thickness should be ~ 68.6 nm. The TiO_x in Fig. 6-2-6(a) is thicker as compared to Fig. 6-1-11. This may be due to the more oxygen has been incorporated in the initial TiO_x when the sample was exposed to many pulses of laser annealing under the normal ambient. The growth mechanism of Fig. 6-2-6 is similar to the case of single-pulsed laser annealing at 0.3 J/cm^2 .

Figure 6-2-5 XTEM of the Ti/Co/Si system without PAI layer after 20 pulses of laser annealing at 0.2 J/cm^2 .

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Figure 6-2-6 (a) XTEM and (b) HRTEM of the Ti/Co/Si system with PAI after 20 pulses of laser annealing at 0.2 J/cm^2 .

Sheet Resistance

Figures 6-2-7 and 6-2-8 demonstrate the comparison of the sheet resistance for single- and multiple-pulsed laser annealed samples for the PAI and non-PAI case at 0.2 J/cm^2 and 0.3 J/cm^2 , respectively.

In Fig. 6-2-7, it can be observed that the sheet resistances for the samples without PAI are low for the samples annealed with 3 pulses and below. The resistances are nearly equivalent to the sheet resistance of the as-deposited sample. When the number of pulse was increased above 5, the sheet resistance increases and it follows the trend of the PAI samples shown in Fig. 6-2-7. Therefore, it can be implied that melting has occurred when 5 pulses or above were used for the samples without PAI. After 5 pulses of laser annealing, the sheet resistance of the non-PAI samples saturates at around $43 \text{ } \Omega/\square$.

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Figure 6-2-7 Sheet resistances for multiple-pulsed laser-annealed Ti/Co/Si samples with and without PAI at 0.2 J/cm².

Figure 6-2-8 Sheet resistances for multiple-pulsed laser-annealed Ti/Co/Si samples with and without PAI at 0.3 J/cm².

For the 0.3 J/cm² fluence, melting has been occurred regardless the number of pulses (see Section 6.1 for one-pulsed annealing results). Hence, the sheet resistances of PAI and non-PAI are high for the first few pulses and begins to decrease at 10 pulses and beyond. For both with PAI and without PAI, the sheet resistance reaches a threshold limit as the number of pulses

increased to 100, reaching a value observed for single-pulsed laser annealing. This implies that even with the further increase in the number of pulse, the Co atoms can not be driven further into the substrate, limiting the growth of silicide and maintaining the thickness of silicide.

The sheet resistances of the laser-annealed PAI and non-PAI samples have the same performance from 1 pulse to 100 pulses for both fluences of 0.2 and 0.3 J/cm². However, the sheet resistance of the PAI samples is lower than that of the non-PAI samples for above 10 pulses indicating that thicker silicide is formed for the PAI samples. The XTEM results shown in Fig. 6-2-6 shows a thicker silicide formed on the PAI samples as compared to that of the non-PAI sample (Fig. 6-2-5), consisting of amorphous and polycrystalline CoTi silicide.

The deviation of the sheet resistance for the same laser annealing conditions (e.g. the value at 10 pulses for 0.2 J/cm² and 5 pulses for 0.3 J/cm²) is due to the variation in the laser distribution [79] of about 10% over the 2.5 mm × 2.5 mm irradiated area.

6.3 Discussion

Based on the study of single-pulsed and multiple-pulsed laser annealing of Ti-capped Co/Si system with and without PAI, it can be seen that the Ti cap has played an important role in transforming the silicide growth mechanisms from crystallization to amorphous phase. Neither single pulse at high fluences nor multiple pulses at low fluences can transform the amorphous phase CoTi into polycrystalline. Instead, in melted solution, the diffusion of Ti atoms is proportional to the laser fluence. The formation of the amorphous phase due to the presence of Ti has contributed to high sheet resistance.

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The Ti and Co once melted can diffuse a few hundreds angstrom within nanosecond of period. A reference can be made by investigating the diffusion length of Co and Ti during their melting. The diffusion length at molten phase can be found using the relationship shown in equation (6.1) with the assumption that the time taken for solidification is longer than the laser pulse, which was 23 ns. Table 6-3-1 lists the thermodynamic properties required for the calculation of diffusion length.

$$L=\sqrt{D\tau}$$
 (6.1)

where L is the diffusion length, D is the diffusivity and τ is the duration time. The diffusivity can be found by using equation (6.2),

$$D = D_o \exp(-\frac{Q}{kT})$$
 (6.2)

where D_o is a proportionality constant, Q is the activation energy and k is the Boltzman constant.

Table 6-3-1 Thermodynamic properties of Co and Ti [4, 87].

	Co	Ti
Activation energy (eV)	2.8	1.8
Proportional constant (cm ² /s)	9.2×10 ⁻⁴	7.2×10 ⁻⁴
Diffusivity in Si (cm ² /s)	9.59×10 ⁻⁴	5×10 ⁻¹⁰
Diffusion length in molten phase (nm)	~47	~40

From Table 6-3-1, the diffusion lengths of Co and Ti are estimated to be about 47 nm and 40 nm, respectively, during melting, which are comparable to the atomic distribution profiles shown by AES (e.g. depth profiles shown by 0.3 J/cm²).

In this experiment, Ti can be considered as an impurity in Co silicidation as it has influenced the thermodynamic and kinetic growth of Co silicide. According to Hume-Rothery [88], Ti is insoluble in CoSi₂. Two elements are soluble (or miscible) if they have the same crystallographic

structure and if their lattice parameter differs by less than 15%. Since CoSi_2 has a face-centered cubic CaF_2 structure, which is different from Ti i.e., closed-packed hexagonal structure. Henceforth, there are no changes in the CoSi_2 nucleation temperature caused by effects of mixing entropy. Nevertheless, changes in the nucleation barrier due to surface energy effects and variations in enthalpy are possible, since the presence of Ti may change the interfacial and/or grain boundary energy [89, 90].

Moreover, the distribution of a large amount of Ti in the CoTiSi liquid can cause the formation of amorphous silicide phase. This is because dominant Si-Ti bonds may have formed due to the largely negative heat of mixing in this large composition range of Ti (i.e., above 23% atomic concentration for solid-state reaction) [80]. Besides, the heat of formation for amorphous CoTi silicide is estimated to be lower than pure CoSi_2 [22, 91]. Based on the EDX results that have been discussed in Sections 6.1 and 6.2, the amorphous phase CoTi silicide starts to form when the composition of Ti is more than 5% of the atomic percentage among the elements. In Ti-capped Co/Si system, CoSi_2 in the (111) plane was normally detected by XRD. This is attributed to the lowest interface energy of (111) CoSi_2 /(111)Si [75, 92].

In the study of single-pulsed laser annealing, the melting threshold occurs around 0.25 J/cm^2 for the Ti/Co/Si system without PAI. For the system with PAI, the melting threshold occurs at 0.2 J/cm^2 , and an explosive crystallization has been observed for this sample, indicating earlier silicidation has taken place for the PAI samples. For 0.3 J/cm^2 , the melt front is suspected to have exceeded the interface of the PAI/substrate, resulting in thicker CoTi silicide compared to the non-PAI case. Same phenomenon was observed in

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multiple-pulsed laser annealing. The samples with PAI show thicker silicide layer compared to that without PAI. This is due to the poor thermal conductivity of amorphous Si compared to single crystal Si [85]. Although the latent heat of fusion for amorphous Si is less than single crystal Si, a large amount of the heat may have been trapped and cause the melt front to propagate further into the substrate [84].

The control of fluence in laser-induced silicidation is important to control the silicide thickness. In this project, high fluence has been perceived from 0.4 to 0.7 J/cm² whereas low fluence is from 0.2 to 0.3 J/cm². It is found that high fluence leads to thick silicide formation whereas low fluence can form silicide not exceeding 70 nm. The adoption of low fluence can also prevent interface roughening between silicide/substrate, which is due to constitutional supercooling.

6.4 Summary

A transition from polycrystalline to amorphous CoTi silicide formation has been observed in the molten region where the Ti atomic concentration is more than 5%. This is because of the insolubility of Ti in CoSi₂, large negative heat of mixing with the presence of Ti or/and the rapid quenching rate of the supercooled liquid. Neither single pulse at high fluences nor multiple pulses at low fluences can transform the amorphous phase CoTi into polycrystalline. The PAI samples have shown the formation of thicker silicide compared to the non-PAI samples for the same laser annealing condition.

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7.1 Study of Single-pulsed Laser Annealing

Experimental

A 13 nm Co layer was deposited, followed by the deposition of a 20 nm TiN layer using DC magnetron sputtering without breaking vacuum on blanket Si substrate with and without a 50 nm PAI layer. In this experiment, a single-pulsed laser in an energy range of 0.2 to 0.7 J/cm² was implemented.

Phase Analysis

Figure 7-1-1 shows the XRD spectra of a TiN/Co/Si system without PAI after a single-pulsed laser annealing for a fluence range of 0.2 to 0.7 J/cm² at an incident grazing angle of 1°. It can be seen that no peak corresponding to silicide phase is identified for fluence between 0.2 and 0.4 J/cm². A peak at ~29.1° that corresponds to CoSi₂ in the (111) plane begins to appear when a fluence above 0.4 J/cm² was used. The intensity of the silicide peak becomes stronger for increasing fluence. The XRD peak at ~42.6° corresponds to TiN in the (200) plane. Hence, it is suspected that the capping layer still stay intact after the exposure to the laser fluence.

Figure 7-1-2 demonstrates the XRD spectra of a TiN/Co/Si system with a 50 nm PAI layer after a single-pulsed LTA for 0.4 to 0.7 J/cm² at an incident grazing angle of 1°. For 0.2 to 0.3 J/cm², there is no Co silicide peak being detected. The XRD peak which corresponds to the CoSi₂ (111) starts to appear at 0.4 J/cm². The silicidation of the PAI samples takes place at 0.1 J/cm²

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fluence lower than that of the samples without PAI. The existence of the capping layer can be ascertained by the peak at 42.6° or/and 36.6° .

Figure 7-1-1 XRD spectra of a TiN/Co/Si system without PAI after a single-pulsed laser annealing for a fluence range of 0.2 to 0.7 J/cm².

Figure 7-1-2 XRD spectra of a TiN/Co/Si system with PAI after a single-pulsed laser annealing for fluence 0.4, 0.5, 0.6, and 0.7 J/cm².

Depth Profile Analysis

To examine the atomic distribution after LTA, AES was carried out for the conditions of 0.2, 0.5, and 0.7 J/cm² for the TiN/Co/Si system with 50nm PAI. The AES profile of the as-deposited sample before annealing is shown in Fig. 7-1-3(a) for comparison. The distribution of atomic concentration after 0.2, 0.5, and 0.7 J/cm² of LTA are shown in Figs. 7-1-3(b), (c), and (d), respectively. It can be seen that the TiN-capping layer still stays intact for each laser annealing condition. For 0.2 J/cm², the onset melting of amorphous Si has taken place (the microstructure will be discussed in a latter part).

For 0.5 J/cm² to 0.7 J/cm², the melting of Co, whole amorphous Si (for PAI sample), or/and part of Si substrate might have occurred. This can be confirmed by the interdiffusion and intermixing of Co and Si shown by AES spectra in Figs. 7-1-3(c)-(d). For the fluence of 0.7 J/cm², a deeper melt depth was resulted. More Si atoms have taken part in the atomic interdiffusion in the liquid phase and a nearly 1:2 of Co:Si ratio has been achieved after solidification.

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Figure 7-1-3 AES spectra of a TiN/Co/Si system with PAI (a) before annealing and after a single-pulsed laser annealing at (b) 0.2, (c) 0.5, and (d) 0.7 J/cm².

Figure 7-1-4 shows the AES spectra of a TiN/Co/Si system without PAI after a single-pulsed laser annealing at 0.2 J/cm^2 . Comparing to the Fig. 7-1-3(b), interdiffusion of Co and Si atoms at the interface can be seen for the non-PAI sample whereas The nearly whole Co layer might have melt and intermixed with Si for the PAI sample.

Figure 7-1-4 AES spectra of a TiN/Co/Si system without PAI after a single-pulsed laser annealing at 0.2 J/cm^2 .

Microstructure Analysis

Figure 7-1-5 shows the microstructures of the TiN/Co/Si system with PAI after a single-pulsed laser annealing at 0.2 J/cm^2 while the inset shows the XTEM micrograph of an as-deposited sample. It can be seen that the 20 nm TiN layer stays intact but has deformed. A bi-layered microstructures can be observed (excluding the TiN layer and amorphous Si). The top layer in dark contrast is the unreacted polycrystalline Co of $\sim 5.4 \text{ nm}$. The bottom layer is the intermixed layer of Co and Si atoms, and its thickness is $\sim 22 \text{ nm}$. A random distribution of the columnar grain structures can be observed in the intermixed layer, indicating crystallization has taken place after solidification. The

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unreacted Co can be ascertained by the XTEM of as-deposited sample, having the same contrast as the pre-annealed Co layer.

Figure 7-1-5 XTEM of a TiN/Co/Si system with PAI after a single-pulsed laser thermal annealing at 0.2 J/cm^2 . The inset shows the microstructures of an as-deposited sample.

The possible growth mechanism for the formation of microstructures shown in Fig. 7-1-5 is as follows. When a laser pulse was irradiated on the sample, the heat is just enough to melt the amorphous Si layer that is near to the surface without melting the Co. This is feasible since the melting temperature of Co and amorphous Si are 1768 K and 1420 K (see Table 5-1-1), respectively. During the melting of amorphous Si, the Co atoms that supposedly stay intact have been induced to diffuse into the molten phase of Si since the solute atoms prefer to stay in liquid phase than in solid phase. Hence, the interdiffusion and intermix of Co and Si atoms in the liquid phase have been resulted. At the instance of freezing, the undercooled intermixed layer solidifies from the liquid/amorphous Si interface, and subsequently this has

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suppressed the Co atoms in the unreacted Co layer from being further diffused into the molten intermixed layer.

The microstructures of the TiN/Co/Si system with PAI after single-pulsed laser annealing at 0.7 J/cm^2 are given in Figure 7-1-6. A few layers can be identified from Fig. 7-1-6(a): the top layer is TiN and the bottom layer is polycrystalline Co silicide. Location A and B in Fig. 7-1-6(a) show different microstructures, in which the TiN layer at A thinner than that at B. This is due to partial melting of the TiN layer at A. Besides, a thin residual amorphous Co silicide is observed at A just underneath the TiN layer. Although the Co silicide layer is polycrystalline as observed from Fig. 7-1-6(a), a highly textured Co silicide layer with defects oriented in the (111) direction is obtained in HRTEM of Figs. 7-1-6(b), (c), and (d). Their corresponding elemental compositions are shown in Fig. 7-1-6(a). The EDX analysis shows only the existence of Ti and Si without any presence of N for the laser-annealed TiN. An EELS experiment was carried out to ensure the presence of TiN capping layer (see Fig. 7-1-7). A thickness comparison between the XTEM (Fig. 7-1-6(a)) and AES depth profile (see Fig. 7-1-3(d)) is given in Table 7-1-1, assuming location A and B shown in Fig. 7-1-6(a) have the same thickness of silicide. Both analyses give the similar results. The estimated thickness of Co silicide obtained from XTEM is about 120 nm. However, the silicide thickness obtained from AES is about 140 nm. This discrepancy could be due to the sample calibration that was meant for SiO_2 .

When the laser pulse was irradiated on the TiN surface, the laser energy is high enough to melt the TiN capping layer partially although TiN has a very high melting temperature. SLIM has shown that the surface temperature can

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exceed the melting temperature of TiN (3203 K) when high fluence of 0.7 J/cm^2 is used. The heat energy is high enough to cause the melting of the Co and PAI layer.

Figure 7-1-6 XTEM of a TiN/Co/Si system with PAI after a single-pulsed LTA at 0.7 J/cm^2 , presented from low to high magnifications from (a) to (d).

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Table 7-1-1 Comparison of thickness obtained from XTEM and AES for the TiN/Co/Si system with PAI after a single-pulsed annealing at 0.7 J/cm².

Layer	XTEM	AES	
	Estimated thickness (nm)	Range of sputtering time (minute)	Estimated thickness (nm)
TiN	20	0 to 2	20
Highly textured CoTi silicide	120	2 to 16	140
Total silicide thickness exclude TiN	120		140

Figure 7-1-7 (a) EELS elemental mapping of nitrogen for a TiN capping layer. (b) The corresponding XTEM of (a).

A rough interface of the silicide and substrate (see Figs. 7-1-6(c) and (d)) can be observed. This rough interface has been resulted by CSC since CSC is likely to occur at high fluence [39]. This further implies that the formation of Co silicide is through crystallization of liquid phase. The dark contrast of defects that resemble stems and branches can be attributed to twinning [18]. It can be seen that defects have grown from the nucleation sites at the silicide/substrate interface and orient in the (111) direction. The growth of this highly textured Co silicide has been encountered in Ti/Co/Si sample after a single-pulsed laser annealing at 0.6 J/cm² [93]. This phenomenon happens due

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to the segregation of the Co solute atoms during CSC and later forms along the (111) direction which has the lowest interface energy. Hence, Co silicide mainly grows along the (111) Si substrate upon freezing. The dark contrast of the textured Co silicide shown in Figs. 7-1-6(c) and (d), corresponds to a higher Co concentration. This has been confirmed by the EELS data (Fig. 7-1-8).

When the solidification front propagates toward the surface near Location A shown in Fig. 7-1-6(a), the thermodynamic of crystallization has been affected by the presence of Ti and this has been discussed in Chapter 6. The dissolution of TiN is believed to have led to the Ti distribution at the region above which the TiN capping layer has partially melted.

Figure 7-1-8 (a) EELS elemental mapping of Co of a section of the highly textured Co silicide layer for TiN/Co/Si after annealing at 0.7 J/cm^2 . (b) The corresponding XTEM of (a).

Figures 7-1-9(a) and (b) show the bright field and dark field, respectively of a TEM plan view of TiN/Co/Si with PAI after a single-pulsed laser annealing at 0.7 J/cm^2 . It can be seen that the average size of the Co silicide grains is 15–65 nm.

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To further confirm the formation of the Co silicide phase, a diffraction pattern analysis was carried out as shown in Fig. 7-1-10(a). Fig. 7-1-10(b) shows the electron diffraction of Si. The phases were investigated by analyzing the electron diffraction pattern in Fig. 7-1-10(a) with respect to the Si reference. The analysis of the diffraction pattern is tabulated in Table 7-1-2. The results have confirmed the presence of CoSi_2 , TiSi and TiN. The formation of TiSi may be due to the dissolution of Ti from the TiN layer. The presence of TiN phase has confirmed that the capping layer still stays intact although it has partially melted.

Figure 7-1-9 (a) Bright field and (b) dark field planar TEM of a TiN/Co/Si system with PAI after annealing at 0.7 J/cm^2 .

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Figure 7-1-10 (a) Electron diffraction pattern of a TiN/Co/Si system with PAI after single-pulsed laser annealing at 0.7 J/cm². (b) Si reference.

Table 7-1-2 Analysis of the diffraction pattern for a (a) Si reference (b) TiN/Co/Si after annealing at 0.7 J/cm².

(a) Si reference

a	Measured r (cm)	h k l	Calculated d (Å)	rd=LW
5.43	5.05	2 0 0	2.715	13.71075

(b) Co silicide layer

Measured r (cm)	Derived d (Å)	h k l	Phase
5.65	2.4267	1 1 1	TiN
7.0	1.9587	1 1 2	TiSi
7.48	1.8330	2 2 0	CoSi₂
8.55	1.6036	3 1 1	CoSi₂

Surface Morphology Analysis

The surface topography of a TiN/Co/Si system with PAI after a single-pulsed laser annealing at 0.2 and 0.7 J/cm² was examined as shown in Figs. 7-1-11 and 7-1-12, respectively. It can be seen that a “ripple-like” pattern of the TiN surface was formed after single-pulsed laser irradiation. The RMS (root mean square) of the surface roughness for 0.2 and 0.7 J/cm² is 17.69 nm and 22.91 nm, respectively. Hence, a higher fluence annealing leads to a rougher surface.

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Figure 7-1-11 (a) 2-dimensional and (b) 3-dimensional AFM view for TiN/Co/Si with PAI after a single-pulsed laser annealing at 0.2 J/cm². The RMS roughness is 17.69 nm.

Figure 7-1-12 (a) 2-dimensional and (b) 3-dimensional AFM view for TiN/Co/Si with PAI after a single-pulsed laser annealing at 0.7 J/cm^2 . The RMS roughness is 22.91 nm .

Sheet Resistance

Figure 7-1-13 shows the comparison of sheet resistance between the laser-annealed TiN/Co/Si system with PAI and without PAI. The sheet resistance of the as-deposited sample before annealing is about $13.6 \text{ } \Omega/\square$. Overall, a similar trend of sheet resistance can be observed for PAI and non-PAI sample.

Both PAI and non-PAI samples show higher sheet resistance for 0.2 J/cm^2 than that of the as-deposited sample. This is because the Co atoms that diffuse into the liquid Si, might not able to form the substitutional solution during the solidification for the PAI sample. For the non-PAI sample, solid-state interface diffusion might have taken place as shown in Fig. 7-1-4. Both samples have been confirmed by the XRD spectra, in which no Co silicide peak was detected.

Although there was a difficulty in detecting Co silicide phase by XRD as a proper stoichiometry of Co silicide is hardly achieved by single-pulsed LTA, a weak XRD peak that infers to Co_2Si was detected for the PAI sample at

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0.4 J/cm² shown in Fig. 7-1-2. This implies that complete melting of the Co and amorphous Si layer might have taken place. When a fluence range from 0.5 to 0.7 J/cm² was used, a decrease in the sheet resistance can be observed. It might be due to the formation of metastable phase that contain partially amorphous or/and polycrystalline silicide [79]. This is similar to the change of resistivity that has been reported for solid-state annealing, where the resistivity of various phases are different at different temperature (i.e. $\sim 70 \mu\Omega \text{ cm}$ for Co₂Si, 100-150 $\mu\Omega \text{ cm}$ for CoSi, and 14-17 $\mu\Omega \text{ cm}$ for CoSi₂) [94]. Hence, the sheet resistance depends on the amount of laser heat that applies to the system. In other words, the higher the fluence, the more it can promote the interdiffusion. For the PAI sample, a single-pulsed LTA at 0.7 J/cm² has caused the whole solidified layer to crystallize, resulting in a 32 $\Omega/\square$ sheet resistance, which was the lowest value.

Figure 7-1-13 Sheet resistance of a TiN/Co/Si system with and without PAI after a single-pulsed laser annealing for a range of fluence from 0.2 to 0.7 J/cm².

7.2 Study of Multiple-pulsed Laser Annealing

Experimental

A 13 nm Co layer was deposited, followed by the deposition of a 20 nm TiN layer using DC magnetron sputtering without breaking vacuum on blanket Si substrate with and without 50 nm PAI. In this experiment, multiple pulsed-laser annealing at low fluence (i.e., 0.2, 0.25 and 0.3 J/cm²) was implemented in order to obtain thin silicide.

Phase Analysis

The phase analysis of a TiN/Co/Si system without PAI after laser annealing for 5, 10, 20, and 50 pulses at 0.2 J/cm² was investigated as shown in Fig. 7-2-1. It can be seen that as the number of pulse increases to above 5, a weak Co silicide peak at ~29° was detected. Besides, another XRD peak at ~45.8° is discovered for 5, 10, 20, and 50 pulses. This peak corresponds to the (210) plane of CoSi.

Fig. 7-2-2 shows the XRD spectra of a TiN/Co/Si system without PAI after multiple-pulsed laser annealing at 0.3 J/cm². With higher laser energy density, there is a tremendous increase in the peak intensity for CoSi₂ in the (111) plane. Furthermore, it can be seen that the intensity of the peak is proportional with the number of pulses. Therefore, a multiple-pulsed laser annealing at 0.3 J/cm² has caused the melting of Co and Si. The growth of Co₂Si and CoSi has been suppressed since no peak is observed for these phases.

Figure 7-2-1 XRD spectra of a TiN/Co/Si system without PAI after multiple-pulsed laser annealing at 0.2 J/cm².

Figure 7-2-2 XRD spectra of a TiN/Co/Si system without PAI after multiple-pulsed laser annealing at 0.3 J/cm².

The phase analysis of silicidation on a TiN/Co/Si system with PAI after multiple-pulsed laser annealing at 0.2 J/cm² is given in Fig. 7-2-3. The XRD

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spectra show that apart from the strong CoSi_2 peak at $\sim 29^\circ$, the CoSi and CoSi_2 peak at $\sim 46^\circ$ and $\sim 48.2^\circ$, respectively are observed. These two peaks correspond to the (210) and (220) plane, respectively.

Figure 7-2-4 shows the XRD spectra of a TiN/Co/Si system with PAI after multiple-pulsed laser annealing at 0.3 J/cm^2 . Similarly, the XRD peak of CoSi_2 in the (111) plane was detected for each condition. The XRD peak at $\sim 55.5^\circ$ corresponding to Si (200) was detected for 10 pulses and above.

Figure 7-2-3 XRD spectra of a TiN/Co/Si system with PAI after multiple-pulsed laser annealing at 0.2 J/cm^2 .

Figure 7-2-4 XRD spectra of a TiN/Co/Si system with PAI after multiple-pulsed laser annealing at 0.3 J/cm^2 .

Depth Profile Analysis

A comparison in the atomic distribution after 20 pulses of laser annealing for the TiN/Co/Si system without PAI and with PAI was made, and the results are shown in Figs. 7-2-5 and 7-2-6, respectively. The capping layer stays intact after multiple pulses. Between the non-PAI and PAI case, a larger Co distribution is observed for the latter. This can be illustrated by the Co tail, where it ends at about 8.5 minutes of the sputtering time for PAI whereas it ends at about 7.5 minutes of sputtering time for non-PAI. It can be seen from Fig. 7-2-6, more Co atoms have been driven by the laser and intermix with Si.

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Figure 7-2-5 AES spectra of a TiN/Co/Si system without PAI after 20 pulses of laser annealing at 0.2 J/cm^2 .

Figure 7-2-6 AES spectra of a TiN/Co/Si system with PAI after 20 pulses of laser annealing at 0.2 J/cm^2 .

Figures 7-2-7(a) and (b) show the depth profiles of a TiN/Co/Si system without PAI after 50 pulses of laser annealing at 0.2 and 0.3 J/cm^2 , respectively. It can be seen from Fig. 7-2-7(a), the depth profile of silicide ends at around 8.5 minutes of the sputtering time, and it is comparable with the silicide thickness shown in Fig. 7-2-6. For a higher fluence at 0.3 J/cm^2 , an increase in the melt depth has been resulted.

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Hence, the adoption of lower fluence with multiple-pulsed annealing can form silicide without sacrificing a thinner silicide. Although the use of higher fluence can form silicide easily, a compromise on a thicker silicide depth has to be made.

Figure 7-2-7 AES spectra of a TiN/Co/Si system without PAI after (a) 50 pulses of laser annealing at (a) 0.2 and (b) 0.3 J/cm².

Microstructural Analysis

Figures 7-2-8(a) and (b) show the XTEM micrographs of a TiN/Co/Si system without PAI after 20 pulses of laser annealing at 0.2 J/cm². It can be

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seen that the TiN capping stays intact but its surface is not uniform. Two distinct microstructural regions are formed, i.e., amorphous Co silicide and polycrystalline Co silicide. Columnar grain structures can be observed in the polycrystalline Co silicide. The atomic concentration of each phase of Co silicide is given in Fig. 7-2-8(b). A 1:2 ratio of Co:Si can be seen for the polycrystalline Co silicide layer. Table 7-2-1 illustrates the comparison of the thickness obtained from XTEM (Fig. 7-2-8(b)) and AES (Fig. 7-2-5).

Figure 7-2-8 (a) Low and (b) high magnification XTEM of a TiN/Co/Si system without PAI layer after 20 pulses of laser annealing at 0.2 J/cm².

Table 7-2-1 Comparison of the thickness obtained from XTEM and AES for the TiN/Co/Si system without PAI after 20 pulses of laser annealing at 0.2 J/cm².

Layer	XTEM	AES	
	Estimated thickness (nm)	Range of sputtering time (minute)	Estimated thickness (nm)
TiN	20	0 to 2	20
α-Co silicide	20	2 to 8	60
Poly-Co silicide	35		
Total silicide thickness exclude TiN	55		60

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The interface between the silicide and substrate is sharp. This is believed that with increasing the number of pulses, the mixing of Co and Si atoms is more distinct [38] and a more uniform composition of intermixed layer can be achieved by multiple shots of irradiation at the same fluence [79]. Since the Co atoms can propagate to a depth of ~55 nm, hence melting has occurred prior the growth of Co silicide. This diffusion length is only achievable in liquid phase (that has been discussed in Section 6.3). Even though a single pulse at 0.2 J/cm^2 might not show melting in the sample without PAI, melting may have taken place during the subsequent pulses of LTA. This is possible since the reflectivity of the TiN would reduce due to the influence of scattering. The scattering of electron has been resulted by the change of surface morphology, in which the TiN surface has become rougher when more laser pulses were irradiated [95]. The formation of amorphous Co silicide might be due to the rapid freezing of undercooled liquid.

Figures 7-2-9(a) and (b) show the XTEM micrographs of a TiN/Co/Si system with PAI after 20 pulses of laser annealing at 0.2 J/cm^2 . It can be seen that the TiN capping stays intact. Two different microstructures of Co silicide layer are observed, i.e., polycrystalline Co silicide and textured Co silicide.

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Figure 7-2-9 (a) Low and (b) high magnification XTEM of a TiN/Co/Si system with PAI layer after 20 pulses of laser annealing at 0.2 J/cm².

The textured Co silicide has different grain orientation contrast compared to that of the polycrystalline Co silicide. The atomic concentration of each phase of Co silicide is given in Fig. 7-2-9(b). Table 7-2-2 illustrates the comparison of the thickness obtained from XTEM (Fig. 7-2-9(a)) and AES (Fig. 7-2-6) for the case of 20 pulses of laser annealing at 0.2 J/cm². The interface between the silicide and substrate is not as sharp as non-PAI (Fig. 7-2-8). The presence of PAI has given rise to different microstructures compared to that shown in Fig. 7-2-8.

Table 7-2-2 Comparison of the thickness obtained from XTEM and AES for the TiN/Co/Si system with PAI after 20 pulses of laser annealing at 0.2 J/cm².

Layer	XTEM	AES	
	Estimated thickness (nm)	Range of sputtering time (minute)	Estimated thickness (nm)
TiN	20	0 to 2	20
Poly-Co silicide	51	2 to 8.5	65
Textured Co silicide	12.7		
Total silicide thickness exclude TiN	63.7		65

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A bi-layered structure consists of poly-Co silicide and textured Co-silicide has formed due to explosive crystallization [52, 82]. During the subsequent pulses of LTA, the melt front might have propagated down to a certain depth of PAI layer. The molten Si promotes the interdiffusion and intermix of Co and Si atoms. When the liquid phase starts to solidify, the latent heat liberated from the liquid raises the temperature of the resolidified polycrystalline Co silicide above the melting temperature of amorphous Si (1420 K or even lower [83]). As a result, the liquid/ α -Si interface propagates down to Si substrate, within which liquid phase epitaxy regrowth has taken place forming the textured Co silicide shown in Fig. 7-2-9(a). When the subsequent laser pulses were irradiated on the sample, it is predicted that the latent heat from the resolidified poly-Co silicide is not high enough to raise the melting temperature of the textured Co silicide since the initial amorphous Si has already melted to form Co silicide.

Surface Morphology Analysis

Figure 7-2-10 (a) 2-dimensional and (b) 3-dimensional AFM view for TiN/Co/Si system without PAI after 7 pulses of laser annealing at 0.3 J/cm^2 . The RMS roughness is 22.45 nm.

The surface morphology of the multiple-pulsed laser-annealed samples was carried out and this is given in Fig. 7-2-10. The figure shows the AFM images for the TiN/Co/Si system without PAI layer after 7 pulses of laser annealing at 0.3 J/cm^2 . The ripple-like surface can be seen with a RMS roughness of 22.45 nm. The RMS surface roughness degrades when higher number of pulses was used (see Fig. 7-1-10).

Figures 7-2-11(a) and (b) show the SEM morphology of a TiN/Co/Si system without PAI for 50 pulses of laser annealing at 0.2 and 0.3 J/cm^2 , respectively. Figs. 7-2-12(a) and (b) show the surface morphology of a TiN/Co/Si system with PAI for 50 pulses of laser annealing at 0.2 and 0.3 J/cm^2 , respectively. Both non-PAI and PAI sample show pinhole formation for 50 pulses of LTA at 0.3 J/cm^2 . Prior the pinhole formation, the TiN has endured thermal shock due to the rapid heating and rapid cooling. The cracks caused by thermal shock, have been observed for 50 pulses of LTA at 0.2 J/cm^2 . Besides, the degree of the ripple-like surface is more severe for the PAI sample than the non-PAI samples. The possible reason is that the thermal

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expansion mismatch between the TiN and crystalline Si is slightly lower than that between the TiN and amorphous Si (see Table 5-1-1). This is because the linear thermal expansion coefficient of amorphous Si is lower than single crystal Si [96].

Figure 7-2-11 SEM of a TiN/Co/Si system without PAI for 50 pulses of laser annealing at (a) 0.2 and (b) 0.3 J/cm² (I: low magnification, II: high magnification).

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Figure 7-2-12 SEM of a TiN/Co/Si system with PAI for 50 pulses of laser annealing at (a) 0.2 and (b) 0.3 J/cm² (I: low magnification, II: high magnification).

Sheet Resistance

Figure 7-2-13 shows the comparison of the sheet resistance of the TiN/Co/Si system with and without PAI layer for single- and multiple-pulsed laser annealing at 0.2 J/cm². The PAI and non-PAI samples demonstrate almost the same trend in the sheet resistance, except the non-PAI samples show a delay in the sheet resistance profile. In other words, for PAI, the sheet resistance starts to decrease when 3 pulses were used. Then it increases when more than 7 pulses were used. Whereas for non-PAI, the sheet resistance starts to reduce when 5 pulses were used and shows an increase when 10 pulses were used.

Figure 7-2-13 Sheet resistance of a TiN/Co/Si system with and without PAI layer after single- and multiple-pulsed laser annealing at 0.2 J/cm^2 .

The change in the sheet resistance is speculated due to the compositional change during the transition of different metastable silicide phases for different numbers of laser pulse used. As can be seen from the XRD spectra (Figs. 7-2-1 and 7-2-3), the CoSi_2 peak become stronger when higher number of pulses is used. The CoSi peak was also detected although the intensity is weak. This indicates that the laser-annealed silicides contain different Co silicide phase. Since Co is a fast diffusive specie with respect to Si [47], the formation of Co_2Si may have been suppressed at the instance of annealing instead CoSi phase is formed during the subsequent pulses of LTA. With the continuous supply of Si from PAI or substrate, the CoSi_2 phase grows eventually.

Single pulse at 0.2 J/cm^2 has shown a mild melting of thin amorphous Si layer as shown in the TEM micrograph in Fig. 7-1-5 and was confirmed with the absence of silicide XRD peak. The possible reason that causes a low sheet resistance for 3 pulses is partially due to the melting of PAI which has

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promoted the interdiffusion of Co. This can be confirmed by the XRD spectra in which a weak CoSi_2 peak at $\sim 29^\circ$ has been detected (not included in Fig. 7-2-3). The increase in the sheet resistance for 7 pulses and above may be caused by the surface roughness of silicide or the formation of amorphous metastable phase. The higher number of pulses has yielded a higher RMS value. When the TiN surface roughness increases, the reflectance becomes lower and subsequently the absorption of heat during annealing is enhanced [97].

The absence of the silicide peak in the XRD spectra for 1 and 3 pulses at 0.2 J/cm^2 for non-PAI samples may imply that no melting has taken place. This can be confirmed by the AES shown in Fig. 7-1-4. The high sheet resistance can be attributed to the electron scattering of the metal layer [67, 86]. The presence of silicide phase in the XRD spectra after 5 pulses of LTA, lead to the decrease in the sheet resistance. Hence, 5 pulses of LTA might have promoted the intermixing of Co and Si atoms. This can be confirmed by the presence of the CoSi_2 phase detected by XRD. The sheet resistance for the microstructures shown in Figs. 7-2-8 and 7-2-9 is ~ 36 and $\sim 47 \text{ } \Omega/\square$, respectively. In Fig. 7-2-9, the crystallized Co silicide for the PAI sample supposedly should yield a lower sheet resistance. However, due to the severe ripple-like surface compared to that of non-PAI (as examined by SEM), a high sheet resistance was resulted. The sheet resistance of 50 pulses for the PAI case is a few hundreds ohm/square.

Figure 7-2-14 shows the comparison of the sheet resistance of the TiN/Co/Si system with and without PAI layer for single- and multiple-pulsed laser annealing at 0.3 J/cm^2 . Both PAI and non-PAI case show similar sheet resistance profile as a function of the number of laser pulse. The presence of

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the CoSi_2 phase detected by XRD for both cases indicates the melting of the Co/Si interlayer has taken place. This can be confirmed by the SLIM simulation too. With the melting of the interlayer, the formation of Co silicide is enhanced. The high sheet resistance for the higher number of pulses shown by both PAI and non-PAI samples is due to the degraded surface roughness and pinhole formation.

Figure 7-2-14 Sheet resistance of a TiN/Co/Si system with and without PAI layer after single- and multiple-pulsed laser annealing at 0.3 J/cm^2 (a) in linear scale and (b) log scale.

7.3 Discussion

TiN possesses higher absorption coefficient than Ti under the 248 nm wavelength of light. However, the results presented in Section 7.1 show that a thin intermix layer of Co and Si atoms has been formed in the TiN/Co/Si system with PAI whereas a thick tri-layered structures of amorphous CoTi silicide/polycrystalline CoTi silicide/textured Si has been formed in the Ti/Co/Si system with PAI for a single-pulsed of LTA at 0.2 J/cm^2 .

This may be caused by the adoption of a thicker TiN capping (i.e. 20 nm) and its high melting temperature. Fig. 7-3-1 shows the schematic illustrating the incidence of a laser on TiN capping and the layer is presented by a stack of equivalent thickness (t) for the ease of explanation. The TiN layer is assumed to be homogenous and its thickness t is chosen so that only a small

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fraction of the light is absorbed when passing through the layer. When the laser irradiates on the TiN surface, the photons (with an energy of 5 eV for KrF) penetrate into the TiN layer. Due to the photoelectric effect (see Section 3.1.2) in the first layer, the intensity of photon flux has decreased prior penetrating into the second layer. In the second layer, same fraction of light is absorbed and it causes the amount of photon flux that transmits through the third layer to reduce tremendously. This phenomenon can be described by equation (3.1). Therefore, the intensity of laser passing through a thick TiN decreases with depth.

Figure 7-3-1 Schematic illustrating the incidence of laser on a TiN capping that is represented by a stack of equivalent thickness, t , layer. Note that the length of the arrows decreases when the light propagates indicating the decrease of light intensity.

Henceforth, when the photon flux propagates to the Co layer, the intensity is so low that it just melts a thin layer of amorphous Si without causing explosive crystallization. Therefore, it can be inferred that the thickness of TiN does play a role in light absorption. The heat absorption will be enhanced if thinner TiN capping is used [98].

The pulsed laser annealing on the TiN/Co/Si system with and without PAI has resulted the laser-induced periodic structure [99, 100]. The ripple-like pattern on the surface has been observed regardless the fluence energy or number of pulses. For example, Fig. 7-3-2 shows the XTEM micrograph of a

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TiN/Co/Si system with PAI after single-pulsed laser annealing at 0.2 J/cm^2 . The inset of Fig. 7-3-2 is the enlarged XTEM micrograph of a portion, which has been shown in Fig. 7-1-5. Another example is given in Fig. 7-3-3 and it shows the XTEM micrograph of the TiN/Co/Si system without PAI after 20 pulses of LTA at 0.2 J/cm^2 , which has been shown in Fig. 7-2-8. Fig. 7-3-4 shows the XTEM micrograph of TiN/Co/Si system with PAI after a single-pulsed annealing at 0.7 J/cm^2 . A wave propagation of the surface can be observed from the three micrographs. Furthermore, thicker silicides at Location A have been formed compared to that at Location B.

Figure 7-3-2 XTEM of a TiN/Co/Si system with PAI layer after a single-pulsed laser annealing at 0.2 J/cm^2 .

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Figure 7-3-3 XTEM of a TiN/Co/Si system without PAI layer after 20 pulses of LTA at 0.2 J/cm².

Figure 7-3-4 XTEM of a TiN/Co/Si system with PAI layer after a single-pulsed LTA at 0.7 J/cm².

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Figure 7-3-5 Schematic of the periodic temperature profile for the TiN/Co/Si sample after LTA.

The formation of ripple surface is hypothesized to occur as described below (see Fig. 7-3-5). When the laser beam of $0.25 \times 0.25 \text{ cm}^2$ is irradiated on the TiN surface of a sample, the heat absorbed by the TiN is modulated to have a fixed period that is governed by the two dimensional heat flow. The temperature wave that propagates along the TiN with the fixed period is attenuated as it is continued by the boundaries which are held at the room temperature [74]. As a result, a periodic of temperature wave has been resulted in the TiN capping layer. The temperature wave with high amplitude has caused localized high temperature (i.e., the regions marked as A). This can be confirmed by the partial melting of the TiN at Location A shown in Fig. 7-3-4. As a result, the high temperature distribution has promoted the silicidation at the localized regions.

The possible reason that causes the ripple-like surface is the freezing of the surface waves. Lu *et al.* [100] has reported the pulsed laser annealing has contributed to the freezing of surface wave in the model of SiO_2/Si . Apparently, this model is similar to the TiN/Co/Si systems with and without

PAI, in which the melting temperature of TiN is high and it has a lower thermal conductivity than Si and Co especially when higher fluences are used [60]. Hence, an appropriate of laser fluence can cause the whole or partial melting of Si or/and Co layer and this has been discussed in previous sections. Due to the presence of TiN on the surface of molten phase, the TiN layer oscillates with the molten surface of the substrate simultaneously. During the rapid freezing, the TiN layer renders a restoring force to the surface waves. As a consequence, a ripple-like of surface has been resulted. Another possible factor that causes the formation of the ripple-like surface might be due to resonance excitation as a consequence of laser light absorption. During the laser irradiation, the surface plasmon at the atmosphere/TiN interface resonantly drives another surface plasmon with the same frequency at the TiN/Co interface. As a result, a strong localized resonance at the interface has occurred, leading to an additional enhancement of electron emission. In order to match the phase between the surface plasmon and the laser light, the TiN surface and Co interlayer becomes periodic [101].

The high sheet resistance that is shown in Figs. 7-2-13 and 7-2-14 can be attributed to the surface roughness of the laser-induced TiN/Co/Si system. When more pulses of LTA were used, the sheet resistance becomes higher. These can be explained by the surface morphology study. The degradation in the sheet resistance has been caused by the severe surface roughness and the formation of pinholes in the TiN capping layer. In order to envisage the pinhole formation in Co silicide, TiN stripping by SC1 was carried out for some samples. An AES depth profiling was carried out so that to ensure there

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is no TiN remaining on the surface of Co silicide after the etch back. It was found that the TiN had been totally removed by the wet chemical etch.

Figs. 7-3-6(a) and (b) shows the SEM micrographs of the TiN/Co/Si system without PAI for 50 pulses of LTA at 0.2 and 0.3 J/cm², respectively, after TiN stripping. It can be seen that a pinhole-free Co silicide is observed for 0.2 J/cm² whereas pinholes were found in Co silicide for 0.3 J/cm².

Figure 7-3-6 SEM of a TiN/Co/Si system without PAI layer for 50 pulses of LTA at (a) 0.2 and (b) 0.3 J/cm² after the TiN stripping.

Figure 7-3-7 SEM of a TiN/Co/Si system with PAI layer for 50 pulses of LTA at (a) 0.2 and (b) 0.3 J/cm² after the TiN stripping.

Figs. 7-3-7(a) and (b) show the SEM micrographs of a TiN/Co/Si system with PAI for 50 pulses of LTA at 0.2 and 0.3 J/cm², respectively after

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TiN stripping. Both 0.2 and 0.3 J/cm² have shown pinhole formation in the laser-annealed Co silicide.

From the SEM micrographs, it can be seen that Co silicide has endured the thermal shock prior the pinhole formation. As it has been discussed in the previous section, the crack phenomenon has also been observed on TiN surface layer prior pinhole formation. Hence, it is believed that the laser-annealed TiN/Co/Si system has induced thermal shock in Co silicide.

Figure 7-3-8 illustrates the AFM image of a TiN/Co/Si system without PAI for 50 pulses of LTA at 0.2 J/cm² after TiN stripping. The RMS roughness is 5.89 nm. Fig. 7-3-9 shows a similar AFM image of a TiN/Co/Si system with PAI for 50 pulses of LTA at 0.2 J/cm² after TiN stripping. The RMS roughness is 12.70 nm. Both AFM images show ripple-pattern on the Co silicide surface and a more severe roughness of Co silicide surface has been resulted for the PAI samples.

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Figure 7-3-8 (a) 2-dimensional and (b) 3-dimensional AFM view for TiN/Co/Si sample without PAI for 50 pulses of LTA at 0.2 J/cm^2 after TiN stripping. The RMS roughness is 5.89 nm.

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Figure 7-3-9 (a) 2-dimensional and (b) 3-dimensional AFM view for TiN/Co/Si with PAI for 50 pulses of LTA at 0.2 J/cm^2 after TiN stripping. The RMS roughness is 12.70 nm .

Figure 7-3-10 plots the comparison of the RMS roughness of the TiN/Co/Si system with and without PAI, after multiple-pulsed of LTA at 0.3 J/cm^2 for before and after TiN stripping. Overall, it shows that the surface of the TiN/Co/Si system with PAI has higher roughness than that without PAI.

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Figure 7-3-10 RMS roughness of the TiN/Co/Si system with and without PAI, after multiple-pulsed laser annealing at 0.3 J/cm^2 for before and after TiN stripping.

Figure 7-3-11 Sheet resistance of the TiN/Co/Si system with and without PAI for multiple-pulsed of LTA at 0.2 J/cm^2 after TiN stripping.

Figure 7-3-11 shows the sheet resistance of the TiN/Co/Si system with and without PAI for multiple-pulsed of LTA at 0.2 J/cm^2 after TiN stripping. Again, when the number of pulse increases, the resistance increases too. The sheet resistance after TiN stripping is higher than that of the pre-stripped

samples (see Fig. 7-2-13). Therefore, the laser-induced ripple-pattern on the annealed surface in the TiN-capped Co/Si samples has resulted formation of a rougher surface in Co silicide, contributing to higher sheet resistance values. This is feasible since the TiN is a hard material [95] and has higher linear thermal expansion coefficient compared to Si (Table 5-1-1). During the rapid heating and cooling, the TiN layer has endured thermal shock [67]. As a result, a crack phenomenon has taken place. When more continuous pulses are being irradiated, the regions of crack boundary which has low energy, become recessed and pinholes are formed eventually [70].

The change in the sheet resistance profiles shown in Figs. 7-2-13 and 7-2-14 can be due to the change of the composition of the Co silicide phase. This can be ascertained by the XRD spectra shown in Figs. 7-2-1 to 7-2-4. Besides, the formation of Co silicide induced by pulsed laser annealing depends on the fluence energy and number of pulses. Different microstructures and metastable phases can be obtained with different annealing conditions [79]. As it can be seen from Section 7.2, a bi-layered structure consisting of an amorphous and polycrystalline Co silicide is achieved for the non-PAI sample after 20 pulses of LTA at 0.2 J/cm^2 . In contrast, a nearly full crystallization of Co silicide is obtained for the PAI sample for the same condition.

Figure 7-3-12 Enlarged XRD spectra of TiN/Co/Si system after multiple pulsed laser annealing at 0.3 J/cm^2 .

In addition, the high sheet resistance of silicide may be attributed to stress, which has been induced during silicidation [102]. This can be further confirmed by the XRD spectra shown in Fig. 7-3-12 for a TiN/Co/Si sample after multiple-pulsed laser annealing. The arrows indicate the peak of CoSi_2 in (111) plane taking from the center of the peak [103]. A RTA sample is used as the control sample to investigate the shift of (111) CoSi_2 . The shift of peak is observed and the degree of shift increases as the number of pulses increases. Besides, the peak broadening is observed too compared to the RTA results.

The shift of diffraction peaks and increase in the FWHM can be attributed to stress [103]. Theoretically, the stress in silicide films consists of intrinsic and thermal stress [104]. Intrinsic stress is due to the volume expansion or reduction of the silicide during the silicidation whereas thermal

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stress is due to the difference in thermal expansion coefficient between the Si substrate and the silicide. It is postulated that the transient annealing which is typically a non-equilibrium process might generate an intrinsic stress in Co silicide. The built up intrinsic stress might not be able to relax. The thermal stress can be attributed to a large mismatch of thermal expansion between TiN and Si (the linear thermal expansion coefficient for TiN, Si, and CoSi₂ is $9.35 \times 10^{-6}/\text{K}$, $2.6 \times 10^{-6}/\text{K}$ and $10.4 \times 10^{-6}/\text{K}$, respectively). The stress in Co silicide has been induced by the TiN capping layer during pulsed laser annealing. This can be confirmed by the ripple-like surface and/or pinhole formation shown in the AFM images and SEM micrographs for laser-annealed samples after the stripping of TiN.

Based on the Tables 7-2-1 and 7-2-2, a thick Co silicide thickness has been obtained for the system with PAI for 20 pulses of LTA at 0.2 J/cm^2 . This has been observed for the Ti/Co/Si system too. Hence, a system with PAI can promote the interdiffusion and intermix of Co and Si atoms. This may be caused by its low thermal conductivity, resulting in a large amount of heat being trapped in amorphous Si, since amorphous Si has lower latent heat of fusion [81]. It shows that multiple-pulsed laser annealing can enhance the formation of Co silicide compared to single-pulsed laser annealing. This can be examined from the XTEM micrographs that have been discussed in Section 7.1 and 7.2.

Different sheet resistance performance can be observed for the Ti/Co/Si and TiN/Co/Si system with and without PAI after multiple-pulsed laser annealing at 0.3 J/cm^2 (see Figs. 7-2-14 and 6-2-8). It can be seen that as the number of pulse increases, the sheet resistance of the Ti-capped samples

decreases indicating thicker CoTi silicide formation. In contrast, the sheet resistance of the TiN-capped samples increases tremendously when the number of pulses increases. This is due to a degraded surface roughness and pinhole formation (see Figs. 7-3-6(b) and 7-3-7(b)).

7.4 Summary

For single- and multiple-pulsed LTA, TiN still stays intact but degrades with the presence of severe ripple-like surface. The periodic temperature wave, freezing of surface wave, or/and resonance excitation have caused the ripple-like surface. Formation of pinholes has taken place for higher number of laser pulses. It has been found that the TiN layer is able to endure the laser induced thermal shock prior the formation of pinholes. After stripping away the TiN layer, it has been found that the TiN capping has induced pinhole formation in the formed Co silicide for higher number of laser pulses. Undesirable factors such as severe ripple effect on the Co silicide surface, pinhole formation, presence of different metastable phases with different number of laser pulses, or/and laser-induced stress in Co silicide have led to a high sheet resistance observed from the laser-annealed Co silicide.

Chapter 8 Silicidation of Co/Si System

8.1 Silicidation of Co (13 nm)/Si System

8.1.1 Study of single-pulsed laser annealing

Experimental

A 13 nm Co layer was deposited using DC magnetron sputtering on blanket Si substrate without a PAI layer. In this experiment, a single-pulsed laser annealing in a fluence range of 0.2 to 0.7 J/cm² was conducted.

Phase Analysis

Figure 8-1-1 XRD spectra of Co (13 nm)/Si system after a single-pulsed LTA for a fluence of 0.2 to 0.7 J/cm².

Figure 8-1-1 shows the XRD spectra of a Co/Si system after single-pulsed laser annealing for a fluence range of 0.2 to 0.7 J/cm². It can be seen

that a XRD peak at $\sim 29^\circ$ is observed for 0.4, 0.5, and 0.6 J/cm² and the peak corresponds to CoSi₂ in (111) plane. As the energy density increases, the peak intensity becomes stronger. Since the SLIM simulation (Fig. 5-3-4) shows that the maximum surface temperature is about 1820 K for 0.4 J/cm², hence it is suspected that Co may have just started to melt. This is because the melting temperature of Co is 1768 K (see Table 5-1-1).

Depth Profile Analysis

Figures. 8-1-2(a)-(c) show the AES depth profiles for an as-deposited sample and the laser-annealed Co/Si samples at 0.3 and 0.7 J/cm². The depth profile for 0.3 J/cm² is comparable with the as-deposited sample. Hence, the fluence from 0.2 to 0.3 J/cm² does not provide enough heat for Co to react. This confirms the absence of silicide phase in the XRD spectra. For 0.7 J/cm², a uniform intermix of Co and Si atoms can be observed due to a melting. However, the ratio of Co:Si is not equivalent to 1:2. Since the sputtering rate of Co silicide is 9.7 nm/min, hence the thickness of silicide layer is estimated to be 73 nm.

It is found that the oxygen profiles before and after annealing did not change and did not affect the silicide growth regardless of the laser fluence (see Figs. 8-1-2(a)-(c)). Hence, the oxygen from the annealing ambient has not been involved in the silicidation reaction during the pulsed laser annealing.

(a)

(b)

(c)

Figure 8-1-2 (a) AES of an as-deposited Co (13 nm)/Si system. AES of a Co/Si system after single-pulsed laser annealing at (b) 0.3 and (c) 0.7 J/cm².

Microstructure Analysis

Figure 8-1-3 XTEM of a Co (13 nm)/Si system after a single-pulsed annealing at 0.7 J/cm^2 .

The XTEM micrograph of a Co/Si system after single-pulsed of LTA at 0.7 J/cm^2 is given in Fig. 8-1-3. It shows that a polycrystalline Co silicide of 73 nm has grown. The 33.5 nm layer showing a different contrast is apparently part of the Si substrate which was confirmed by EDX analysis (see Appendix III). The possible reason for seeing the 33.5 nm Si layer is due to the solid phase epitaxy regrowth [34] caused by the crystallization latent heat that propagates down to the Si substrate. As shown by the AES depth profile in Fig. 8-1-2(c), it has a well-intermixed of Co and Si layer and the melt depth shown by the AES results agrees with the thickness observed from the XTEM micrograph. The resistivity of the $\sim 33 \text{ } \Omega/\square$ Co silicide phase is calculated to be $\sim 240 \text{ } \mu\Omega \text{ cm}$, which is higher than the resistivity of CoSi_2 , CoSi , or Co_2Si . The resistivity for CoSi_2 , CoSi and Co_2Si is $14\text{--}17 \text{ } \mu\Omega\text{-cm}$, $100\text{--}150 \text{ } \mu\Omega\text{-cm}$ and $70 \text{ } \mu\Omega\text{-cm}$, respectively [94]. Hence, the Co silicide phase grown may have defects. This may be confirmed by the microstructures analysis shown in Fig.

7-1-6. The native oxide on the Co surface has not impeded the growth of Co silicide during annealing.

Sheet Resistance

The sheet resistance for a Co/Si system after single-pulsed laser annealing is shown in Fig. 8-1-4. The sheet resistance for the as-deposited sample is $13\ \Omega/\square$. The increase in the sheet resistance from 0.2 to 0.4 J/cm² may be due to the electron scattering, which has been discussed in the previous section. When a 0.5 J/cm² was irradiated, the Co has melted and interdiffused with Si. SLIM has shown the onset of the Co melting occurred at 0.4 J/cm². The formation of a thick silicide has resulted the reduction in the sheet resistance for fluence of 0.5 J/cm² and above.

Figure 8-1-4 Sheet resistance of a Co (13 nm)/Si system after single-pulsed laser annealing for a range fluence.

8.1.2 Study of multiple-pulsed laser annealing

The understanding of single-pulsed laser-annealed silicide on the Co/Si system was extended to multiple-pulsed laser annealing. Fig. 8-1-5 shows the XRD spectra of a Co/Si system for 10, 20, 50, and 100 pulses at 0.2 J/cm^2 . It can be seen that the interdiffusion of Co with Si is difficult even though up to 100 pulses of laser was used. A very weak XRD peak at $\sim 46.15^\circ$ is detected at 100 pulses which corresponds to CoSi (210).

Figure 8-1-6 shows the XRD spectra of a Co/Si system after multiple-pulsed laser annealing at 0.3 J/cm^2 . Two XRD peaks at $\sim 29^\circ$ and $\sim 48.3^\circ$ were detected and their peak intensity become stronger when the number of pulse increased. These two peaks correspond to CoSi_2 in the (111) and (220) plane.

Figure 8-1-5 XRD spectra of a Co (13nm)/Si system after multiple-pulsed laser annealing at 0.2 J/cm^2 .

Figure 8-1-6 XRD spectra of a Co (13 nm)/Si system after multiple-pulsed laser annealing at 0.3 J/cm².

Depth Profile Analysis

The depth profile of a Co/Si system after 100 pulses of LTA at 0.2 and 0.3 J/cm² is given in Figs. 8-1-7(a) and (b), respectively. For 0.2 J/cm², the distribution of Co ends at around 5.5 minutes of the sputtering time. Hence, the thickness of Co silicide can be estimated to be 53 nm. A Co:Si ratio of 2:1 was obtained near to the surface of the sample. This explains the presence of Co₂Si phase in XRD spectra in Fig. 8-1-5. For 0.3 J/cm², the distribution of Co ends at around 6 minutes of the sputtering time. The melt depth of Co silicide can be estimated to be 58 nm.

Figure 8-1-7 AES of a Co/Si system for 100 pulses of LTA at (a) 0.2 and (b) 0.3 J/cm².

Sheet Resistance

The comparison in the sheet resistance between 0.2 and 0.3 J/cm² for the multiple-pulsed laser annealing is shown Fig. 8-1-8. The sheet resistance increases as higher number of pulse was used for 0.2 J/cm². In contrast, the sheet resistance decreases when higher number of pulse was used for 0.3 J/cm². The possible reason that causes the increment in the sheet resistance for 0.2 J/cm² is the laser energy is not high enough to promote the interdiffusion of Co

and Si atoms compared to fluence of 0.3 J/cm². Single-pulsed of LTA at 0.2 and 0.3 J/cm² has shown non-melt phenomenon. However, an earlier melting may have occurred for 0.3 J/cm² during the subsequent pulses of annealing. This is possible since the absorption of Co can increase when it is annealed with high temperature [50]. Hence, a full crystallization of Co silicide has been obtained for 100 pulses of LTA at 0.3 J/cm². For 0.2 J/cm², formation of mixed metastable phases might have taken place, contributing to high sheet resistance. The well-intermixed Co and Si layer has confirmed the formation of Co silicide, which contributes to the low sheet resistance.

Figure 8-1-8 Comparison of sheet resistance for multiple-pulsed laser annealing at 0.2 and 0.3 J/cm².

8.2 Silicidation of Co (8 nm)/Si System

Experimental

A thinner cobalt (8 nm) layer was deposited on (100)Si substrate. Based on the results that have been discussed in Section 8.1, multiple-pulsed annealing at 0.3 J/cm² was able to deliver promising results. Hence, in this section, a multiple-pulsed laser annealing at 0.3 J/cm² was implemented for a

thin Co system. AES characterization and sheet resistance measurement were implemented to envisage the interdiffusion and intermix of Co and Si atoms.

Phase Analysis

Figure 8-2-1 XRD spectra of a Co (8 nm)/Si system after 100 pulses of laser annealing at 0.3 J/cm^2 . A RTA-annealed sample is included for comparison.

Figure 8-2-1 shows the grazing incidence XRD spectra at 0.8° for a Co/Si system after 100 pulses of laser annealing at 0.3 J/cm^2 . Although the spectra is weak compared to that of RTA, two peaks at $\sim 29.7^\circ$ and $\sim 48.25^\circ$ corresponds to CoSi_2 in the (111) and (220) plane were detected, respectively. Therefore, it can infer that silicidation has taken place. Nevertheless, the XRD intensity is not as strong as that of the thicker Co (13 nm) using the same annealing condition (see Fig. 8-1-6).

Depth Profile Analysis

(a)

(b)

(c)

Figure 8-2-2 AES of a Co (8 nm)/Si system (a) before annealing, after (b) 50, (c) 150 and (d) 300 pulses of laser annealing at 0.3 J/cm^2 .

Figure 8-2-2 shows the AES of the 8 nm Co before and after annealing for 50, 150 and 300 pulses at 0.3 J/cm^2 . It can be seen that interdiffusion between Co and Si atoms just start to take place at 50 pulses. For both the 150 and 300 pulses, no difference in the depth profile of the Co distribution is observed.

Sheet Resistance

Figures 8-2-3(a) and (b) show the sheet resistance after multiple-pulsed laser annealing at 0.3 J/cm^2 for a Co (8 nm)/Si system with and without a 20 nm PAI layer, respectively. The 20 nm PAI layer was formed by implanting a n-type Si (100) substrate with Si^+ to a dose of $1 \times 10^{15} \text{ cm}^{-2}$ at an energy of 9 keV. The sheet resistance of the as-deposited sample is about $36.2 \text{ } \Omega/\square$.

Both samples with and without PAI show similar sheet resistance results. From Fig. 8-2-3(a), the sheet resistance is about $67 \text{ } \Omega/\square$ for a 10-pulse annealing, then increases to $\sim 91 \text{ } \Omega/\square$ for a 20-pulse annealing. It starts to

decrease when 50 pulses were used. This can be attributed to an onset interdiffusion between the Co and Si atoms as shown in the depth profile for the 50-pulse annealing at 0.3 J/cm^2 shown in Fig. 8-2-2(b). As discussed in Section 8.1, the onset of melting of Co can only occur when a single-pulsed LTA at 0.5 J/cm^2 was used. Hence, 10 to 50-pulse annealing at 0.3 J/cm^2 might just enough to cause the variation in electron scattering. The as-deposited film stacks which are grown by PVD (physical vapor deposition) method exhibits a limited atomic mobility [67, 86]. During the rapid heating, the thermal vibrations from the laser energy cause the Co atoms to be dislodged from the lattice alignment, and this subsequently affects the periodicity of the lattice. As a result, an incoherent scattering of the electron waves has occurred, which can be reflected by a drastic increase of the sheet resistance. Hence, more electron scattering has been resulted when a higher number of laser pulses is irradiated on the sample. When more than 50 pulses of the laser were used, the Co should have started to melt forming thicker silicide. The surface of the samples after annealing have been examined by SEM and no degradation of surface morphology was observed. A similar sheet resistance profiles was obtained for PAI sample shown in Fig. 8-2-3(b).

For both samples with and without PAI, the sheet resistance stabilizes at $\sim 25 \text{ } \Omega/\square$ even the number of pulses was increased to 300. This implies that the Co atoms cannot be driven further into the substrate, limiting the growth and maintaining the thickness of the silicide. Therefore, it can be seen that the 20 nm PAI layer does not play a significant role in improving the silicide formation since the sheet resistance is comparable with that of the samples without PAI.

Figure 8-2-3 Sheet Resistance of a Co (8 nm)/Si system (a) without PAI and (b) with PAI, after multiple-pulsed laser annealing at 0.3 J/cm^2 .

8.3 Discussion

It is found that native oxide on the surface of Co/Si sample does not hinder the silicidation during the pulsed-laser annealing regardless of the fluence and number of pulses. Instead, the native oxide just remains intact without propagating further into the substrate. Besides, the silicidation of Co

(13 nm)/Si system has achieved the lowest sheet resistance among all the samples (see Fig. 8-1-8), including the Ti/Co/Si and TiN/Co/Si samples. Henceforth, 100 pulses of LTA at 0.3 J/cm^2 has shown to be a promising recipe to form Co silicide.

The performance of laser-induced silicidation on thinner Co (8 nm) is not reproducible. It is more difficult to form Co silicide indeed. Fig. 8-3-1 illustrates the depth profile of Co (13 nm)/Si after 10 pulses of LTA at 0.3 J/cm^2 whereas Fig. 8-2-2(b) shows the depth profile of Co (8 nm)/Si after 50 pulses of LTA at 0.3 J/cm^2 . A deeper intermixing layer of Co and Si for the 13 nm Co can be obtained compared to that of the 8 nm Co. Therefore, the growth of Co silicide is not only influenced by number of pulses but also by the amount of the as-deposited Co.

Figure 8-3-1 AES of a Co (13 nm)/Si system after 10 pulses of laser annealing at 0.3 J/cm^2 .

It can be seen from Fig. 8-1-4, the sheet resistance for the thicker Co (13 nm) sample increases when energy density increases from 0.2 to 0.4 J/cm^2 for a single-pulsed LTA. Since no interdiffusion of Co is seen from the AES depth profile for 0.3 J/cm^2 (Fig. 8-1-2(b)), there is no Co interdiffusion with the

metal layer staying intact for laser fluence lower than 0.5 J/cm^2 . Therefore, the increase of sheet resistance is due to more electron scattering when higher fluence of laser pulse was used [67, 86]. It starts to decrease when a laser fluence above 0.4 J/cm^2 was used. This is because interdiffusion of Co and Si has occurred as a result of melting.

For multiple-pulsed LTA of the Co (13 nm) sample, two different sheet resistance performances can be seen for 0.2 and 0.3 J/cm^2 (see Fig. 8-1-8). The sheet resistance for the 0.2 J/cm^2 annealed sample increases with increasing number of pulses. In contrary, the sheet resistance for the 0.3 J/cm^2 annealed samples decreases when higher number of pulses was used. From the depth profile shown in Fig. 8-1-7(a), the Co only starts to interdiffuse and intermix with Si when 100 pulses of LTA at 0.2 J/cm^2 was used. However, a nearly 1:1 intermixing of Co:Si has been achieved for 0.3 J/cm^2 (Fig. 8-1-7 (b)). This is due to an enhanced interdiffusion and intermixing for a higher laser fluence. Hence, the 0.3 J/cm^2 fluence has provided a significant amount of heat to form a thicker silicide compared to 0.2 J/cm^2 . As a result, the sheet resistance decreases when the number of pulses increases for the laser fluence of 0.3 J/cm^2 .

8.4 Summary

The multiple-pulsed laser annealing on a Co/Si system without capping layer has shown the native oxide on the surface of Co layer does not hinder the silicidation. A sheet resistance of $12.5 \text{ } \Omega/\square$ has been obtained in the Co (13 nm)/Si system for 100 pulses of LTA at 0.3 J/cm^2 . However, the result is not producible for the Co (8 nm)/Si system for the same annealing condition. This

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is because the amount of the as-deposited Co film is less and a thinner Co silicide layer has grown.

Chapter 9 Silicidation on Device Structures

9.1 Experimental

In this chapter, the investigation of the electrical performance of the laser-annealed Co silicide was conducted. All the measurements were electrically probed directly onto silicided pads without metallization. Based on the study of 8 nm Co layer on Si substrate shown in Chapter 8, the laser-annealed conditions of ≥ 100 pulses at 0.3 J/cm^2 were used to form the laser-annealed Co silicide. In this experiment, 100, 150, 200, 250, and 300 pulses of laser annealing at 0.3 J/cm^2 were used. After the laser processing, the unreacted Co was chemically removed by using SC1 (chemical combination of NH_4OH , H_2O_2 , and H_2O) prior to the electrical measurement. This is to prevent bridging between the test structures. A RTA sample has been incorporated for comparison. The RTA experiments were performed using a 2-step RTA at 450°C and 825°C for 30 seconds in a N_2 ambient.

9.2 Electrical Characterization

Figures 9-2-1 and 9-2-2 show the sheet resistance of a laser-annealed Co silicide on p+ and n+ active Si with different linewidths, respectively. Table 9-3-1 summarizes the sheet resistance of silicided p+ and n+ Kelvin structures.

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Table 9-2-1 Sheet resistance of silicided (a) p+ and (b) n+ Kelvin structures for different linewidths.

p+ active linewidth (μm)	Rs ($\Omega/\square$)		
	RTA	100 pulses of LTA	300 pulses of LTA
0.15	8.7	33.2	32.5
0.50	9.7	20.6	15.26

(a)

n+ active linewidth (μm)	Rs ($\Omega/\square$)		
	RTA	100 pulses of LTA	300 pulses of LTA
0.15	6.7	27.4	97.8
0.50	6.8	24.2	22.9

(b)

Both figures show that the laser-annealed Co silicide has higher sheet resistance than that of the RTA sample. This may be attributed to the incomplete crystallization of Co silicide. In other words, the microstructures of laser-induced silicide might consist of metastable polycrystalline or/and amorphous Co silicide. For the p+ active regions, 300 pulses of LTA has resulted in a lower sheet resistance compared to 100 pulses of LTA. Similar results have been observed in the study of laser-annealed Co silicide on blanket Si substrate (see Fig. 8-2-3). Similar phenomenon has been observed in Fig. 9-2-2, where the sheet resistance for 300 pulses of LTA is lower than the 100 pulses of LTA, except for the 0.15 μm active linewidth. The discrepancy might be due to the degradation of surface morphology, which will be discussed latter.

Figure 9-2-1 Sheet resistance of laser-annealed Co-silicided p+ Kelvin structure for 0.15 and 0.5 μm linewidth.

Figure 9-2-2 Sheet resistance of laser-annealed Co-silicided n+ Kelvin structure for 0.15 and 0.5 μm linewidth.

The measurement of the reverse bias and forward bias current are to assess the junction leakage current and the Co-silicided diode characteristics, respectively. The junction leakage and forward biased current of the p+/n perimeter intensive diode, n+/p perimeter intensive diode, and p+/n area intensive diode (see details in Chapter 3) are given in Figs. 9-2-3, 9-2-4, and 9-2-5, respectively. The samples with 100 and 300 pulses of LTA were selected

for electrical characterization. A RTA sample is incorporated into the figures. The overall results show that the junction leakage current of the laser-annealed Co silicide for different junction diodes are lower than that of the RTA Co-silicided diode.

Besides, the forward bias currents demonstrate a good diode characteristic with higher drive current compared to that of the RTA sample. In general, the diode current-voltage relationship may be expressed as

$$I = I_s \left[\exp\left(\frac{eV_a}{nkT}\right) - 1 \right] \quad (10.1)$$

where I_s is the ideal reverse saturation current and n is the ideality factor. I_s is a function of the parameters, i.e., hole/electron diffusion coefficients, equilibrium hole/electron concentration in n/p+ regions, and hole/electron diffusion length. Hence, it is suspected that the drive current of laser-annealed Co silicide has been affected by the I_s . In order to investigate the microstructures of laser-annealed Co silicide, XTEM was carried out.

Figure 9-2-3 Reverse and forward bias current of a p+/n perimeter intensive diode for 100 and 300 pulses of LTA at 0.3 J/cm². A RTA-annealed diode is included for comparison.

Figure 9-2-4 Reverse and forward bias current of a n^+/p perimeter intensive diode for 100 and 300 pulses of LTA at 0.3 J/cm^2 .

Figure 9-2-5 Reverse and forward bias current of a p^+/n area intensive diode for 100 and 300 pulses of LTA at 0.3 J/cm^2 .

9.3 Microstructural Analysis

Figures 9-3-1(a)-(d) show the XTEM micrographs of Co-silicided p^+ active for a $0.15 \mu\text{m}$ linewidth after 100 pulses of LTA at 0.3 J/cm^2 . The EDX

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analysis at different locations of Co silicide (Fig. 9-3-1(a)) was carried out and the results are shown in Table 9-3-2. In Fig. 9-3-1(a), a layer of an evaporated and FIB-deposited Pt layer can be observed on top of the Co silicide. The purpose of depositing the layer of Pt is to protect the sample during the TEM sample preparation.

Figure 9-3-1 (a) High and (b) low magnification of XTEM for Co-silicided 0.15 μm p+ active line. The crystalline Co silicide is marked as Δ in (a). (c) and (d) HRTEM of the Co-silicided p+ active after 100 pulses of LTA at 0.3 J/cm², showing the lattice image of Co silicide on a (100) Si substrate. The electron diffraction pattern of crystalline Co silicide is shown in the inset of Fig. (b).

Table 9-3-1 EDX analysis on different locations shown in Figs. 9-3-1(a) and (b).

Location	Component	Atomic ratio
1	Co:Si:O	17.53:67.74:14.73
2	Co:Si	35.50:64.50
3	Co:Si	35.26:64.74
4	Si:O	68.51:30.40
5	Co:Si:O	58.35:4.32:37.33

An EELS elemental mapping of Co was carried out in order to examine the Co distribution and the results are shown in Fig. 9-3-2. It is found that Co was detected on the surface of STI region, which is further away from the active line. No Co atom was detected at the edge of the Si active regions. The EDX results at Location 5, i.e., STI region shown in Fig. 9-3-1(b) indicate the presence of Co on the STI region (see also Table 9-3-1). The compound at Location 5 is Co silicate (CoSi_xO_y) as it consists of Co, Si and O with an atomic percentage of 58.35, 4.32, and 37.33, respectively, which is non-conductive in nature. Besides, an investigation for the possibility of leakage path between the two active regions was carried out and the leakage current is one order of magnitude lower than the results obtained in Figs. 9-2-3 to 9-2-5. This implies that there is no leakage path between the active line and STI regions. In addition, the microstructures analysis demonstrates that Co silicide has formed on the active line. Hence, the I-V curves shown in Figs. 9-2-3, 9-2-4, and 9-2-5 are valid.

Figure 9-3-2 (a) EELS elemental mapping of Co for the Co-silicided $0.15\ \mu\text{m}$ p^+ active line. (b) The corresponding XTEM of (a).

It can be seen from Fig. 9-3-1(a) that the interface of Co silicide is abrupt and smooth. The laser-induced silicide thickness is $\sim 35\ \text{nm}$. As seen from Fig. 9-3-1(b), the expected junction depth (x_j) of the p^+/n diode is $120\ \text{nm}$. Hence, the 100 pulses of LTA at $0.3\ \text{J}/\text{cm}^2$ has resulted a thin layer of Co silicide, explaining the superior junction leakage current shown in Figs. 9-2-3 to 9-2-5. With the application of multiple-pulsed laser annealing, the Co atoms have been driven into the Si substrate. This can be confirmed by the EDX analysis at Location 1, 2, and 3 shown in Fig. 9-3-1(a). High oxygen concentration was detected at Location 1. The initial oxide may contribute to the oxygen concentration.

A HRTEM analysis was carried out to investigate the microstructures of the formed Co silicide layers and this is shown in Figs. 9-3-1(c) and (d). Amorphous and crystalline Co silicide are formed after the multiple-pulsed laser annealing. The Co silicide phase at Location 3 is single crystal, fully coherent, and epitaxial with (100) Si. This has been confirmed by the electron

diffraction pattern shown in the inset of Fig. 9-3-1(d). The growth of the single-crystalline Co silicide is such that its (111) plane is parallel to the (111) plane of the (100) Si substrate, indicating a liquid phase epitaxy regrowth has taken place. Therefore, it is inferred that melting has occurred during the subsequent pulses of LTA. This phenomenon has been observed in the study of multiple-pulsed laser annealing on blanket Si substrate. A non-uniform thickness of Co silicide on the 0.15 μm active line has been observed. This may be attributed to the nucleation site which has taken place at the center of the 0.15 μm line. The presence of the crystalline Co-silicided structure seen in Fig. 9-3-1(c) and (d) confirm the hypothesis. Hence, a thicker layer of Co silicide layer is formed at the center of active line due to a growth in a radial pattern on the very narrow Si line.

Figures 9-3-3(a) and (b) show the XTEM and HRTEM of a Co-silicided 0.5 μm active line. The EDX analysis results at different locations of Co silicide (Fig. 9-3-3(a)) are shown in Table 9-3-3. It can be seen that a thinner Co silicide layer of ~ 26 nm consisting of amorphous and crystalline phase has formed. A nucleation site/seed layer can be observed at Location 3 i.e., indicated by the wedge shown in Fig. 9-3-3(a). The HRTEM micrograph of crystalline Co silicide is shown in Fig. 9-3-3(b). It is believed that the crystalline Co silicide starts to nucleate around the convexity (wedge indicated) and subsequently grows epitaxially to the Si substrate such that the Co silicide (111) plane is parallel to the (111) plane of the (100) Si substrate. This indicates that liquid phase epitaxy regrowth has taken place.

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Figure 9-3-3 (a) XTEM and (b) HRTEM of a Co-silicided 0.50 μm p+ active line after 100 pulses of LTA at 0.3 J/cm². The crystalline Co silicide is marked as Δ in (a) and the lattice image of Co silicide can be observed in (b).

Table 9-3-2 EDX analysis on different locations shown in Figs. 9-3-3(a).

Location	Component	Atomic ratio
1	Co:Si:O	29.50:56.75:13.75
2	Co:Si	41.06:59.94
3	Co:Si	40.61:59.39
4	Si:O	86.40:13.60

By comparing the results collected from the wide and narrow Si lines, a thicker Co silicide is formed on a narrow line. Since the SiO₂ has a poor thermal conductivity compared to Si (the thermal conductivity of SiO₂ and Si are 0.014 and 1.412 W/cm-K, respectively), hence it is suspected that a large amount of heat has been trapped within a smaller line upon laser irradiation. Heat diffusion can only readily take place vertically, via the Si surface or the Si substrate surrounding by the STI. The two dimensional heat confinements can be revealed by the EDX measurements shown at Location 4 for both 0.15 μm and 0.50 μm Si lines (see Figs. 9-3-1(a) and 9-3-2(a)). The EDX analysis has shown the presence of a very high concentration of oxygen in the amorphous Si. As more heat has been trapped in the narrower linewidth, more diffusion of

oxygen from the neighbouring STI into the Si substrate is seen. This is confirmed by more oxygen atoms detected at the corner of the $0.15\ \mu\text{m}$ Si line. Besides, the EDX results show that more Si atoms are present in the laser-induced Co silicidation for narrower active lines compared to wide active lines. Hence, narrower active lines have promoted more formation of Co silicide through the enhancement of heat confinement by the STI [14].

Figure 9-3-4 (a) EELS elemental mapping of Co for the Co-silicided $0.50\ \mu\text{m}$ p^+ active line. (b) The corresponding XTEM of (a).

From Figs. 9-3-1 and 9-3-3, a bi-layered structure has been formed. The structure consists of a crystalline Co silicide at the center of the active line and an amorphous Co silicide around the crystalline Co silicide. It is believed that the crystalline Co silicide nucleate near the centre of active line of the Co silicide/Si interface. In addition, no crystallization is observed at the region near to the STI oxide. The possible growth mechanism for the formation of the amorphous Co silicide is due to a fast solidification velocity as a result of supercooled liquid [81, 82]. The temperature of the supercooled liquid could have fallen below the melting temperature of the amorphous Co silicide. As

discussed in the previous section, the STI region adjacent to the active Si has trapped a large amount of heat during pulsed irradiation. During the solidification, the supercooled liquid is forced to quench into an amorphous phase. As a result, the solidification interface propagates at even higher velocity, resulting the transformation of the crystalline Co silicide into an amorphous phase.

9.4 Discussion

The multiple-pulsed laser-annealing recipe developed at 0.3 J/cm^2 has been implemented into a $0.13 \text{ }\mu\text{m}$ device technology for the formation of Co silicide on patterned wafers. The formed CoSi_x can be confirmed by the sheet resistance measured from n+ and p+ Kelvin Si active structures. Moreover, the sheet resistance is comparable to the results obtained from blanket substrate. The microstructures analysis shows that amorphous and crystalline Co silicides have been formed after the multiple-pulsed of LTA process for 0.15 and $0.50 \text{ }\mu\text{m}$ Si active. Heat confinement phenomenon is more obvious in narrow active lines, in which the formation of thick silicide has been promoted.

The low leakage current of laser-annealed Co-silicided p+/n and n+/p junctions can be attributed to the smooth silicide/Si interface and the formation of thin Co silicide, which have been confirmed by XTEM analysis. This is because the leakage current of shallow junction is very susceptible to the silicide microstructures [107]. In addition, a rough silicide/Si interface can enhance the electric field between the silicide and junction [108, 109]. Henceforth, a high junction leakage current can be resulted if the penetration

depth of silicide into the junction area was severe and/or the interface of silicide/Si was rough.

The growth of crystalline Co silicide which is fully coherent and epitaxial with (100) Si has been achieved using pulsed-laser annealing. In contrast, epitaxy Co silicide can only be obtained by applying a refractory metal interlayer between Co and Si for the RTA silicide [110]. Although multiple-pulsed laser annealing has shown the possibility of forming a good silicide, there are still challenging integration issues that needed to be resolved, which will be discussed in latter part. It can be seen from the results that 100 pulses of LTA at 0.3 J/cm^2 has yet to lead to a complete crystallization of Co silicide. Hence, the laser-annealed recipes still need to be fine-tuned.

Integration challenges encountered during the LTA

The pulsed-laser thermal annealing on the patterned wafer has given rise to some challenges. One of them is the formation of amorphous SiO_2 at the edge of the Si active lines regardless of the linewidths as shown in Figs. 9-3-1 and 9-3-3. This may be attributed to the effect of more severe heat confinement at the corner regions between the STI and active Si lines. Besides, the non-conductive CoSi_xO_y on STI cannot be stripped away by SC1. It is suspected that SiO_2 in STI has reacted with Co. This process is possible since the bandgap energy of SiO_2 (9 eV) is higher than the photon energy of KrF (i.e., 5 eV). In addition, the SiO_2 surface in STI contains a high concentration of impurities and defect due to the S/D implantation. Hence, there is a chance for metallic multiphoton processes and the reaction of Co with broken Si-O bond to occur [106].

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Figures 9-4-1(a) and (b) show low and high magnification of SEM micrographs of STI regions after multiple-pulsed laser annealing. The EDX analysis results at Locations 1 and 2 shown in Fig. 9-4-1(b) are illustrated in Table 9-4-1. It can be seen that the formation of Co silicate cluster and pinhole on the STI regions. No Co was detected by EDX at Location 2. This may be due to the de-lamination of Co silicate from the STI surface. Fig. 9-4-1(c) shows the SEM micrographs of Co-silicided n+ active region after 300 pulses of LTA at 0.3 J/cm^2 . A severe agglomeration can be observed and this might have contributed to high sheet resistance for $0.15 \text{ }\mu\text{m}$ active line shown in Fig. 9-2-2.

(c)

Figure 9-4-1 (a) Low and (b) high magnification of SEM of STI regions after multiple-pulsed laser annealing at 0.3 J/cm^2 . (c) SEM of Co-silicided n^+ active region after 300 pulses of LTA at 0.3 J/cm^2 .

Table 9-4-1 EDX analysis on different locations shown in Figs. 9-4-1(b).

Location	Component	Atomic ratio
1	Co:Si:O	12.78:42.63:44.59
2	Si:O	49.43:50.57

9.5 Summary

The 100 pulses of LTA at 0.3 J/cm^2 has shown the formation of Co silicide on patterned wafers. This has been confirmed by the sheet resistance measurement and microstructures analysis. A nucleation site where the epitaxy Co silicide has grown was observed in the formed amorphous Co silicide after the LTA. The mixed phases of Co silicide might have contributed to high sheet resistance. However, the thin silicide and smooth silicide/substrate interface have contributed to low leakage current. Although multiple-pulsed laser annealing has shown the possibility of forming a good silicide, there are still challenging integration issues that needed to be resolved.

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10.1 Conclusion

TiN and Ti capping layer in laser-annealed Co/Si system has resulted in different growth mechanisms and microstructures of Co silicide. The Ti cap plays an important role in transforming the silicide growth mechanisms from crystallization to amorphous phase. Neither single pulse at high fluences nor multiple pulses at low fluences can transform the amorphous phase CoTi into polycrystalline. The results show that the amorphous phase CoTi silicide starts to form when the composition of Ti is more than 5% of the atomic percentage among the elements. No degradation of surface morphology was observed for the laser-annealed Ti/Co/Si system.

In contrast, the TiN capping layer remains intact for single-pulsed LTA in a fluence range of 0.2 to 0.7 J/cm² and multiple-pulsed LTA at low fluence (i.e., 0.2 to 0.3 J/cm²). A single-pulsed LTA at 0.7 J/cm² has shown partial melting of the TiN capping layer. The TiN layer which does not dissolve has not affected the crystallization of Co silicide as shown in Fig. 7-1-6. However, a ripple-like surface of the TiN layer has been resulted in the laser-annealed TiN/Co/Si system with and without PAI. The ripple-like surface of Co silicide was observed even though the un-reacted Co and TiN layer were stripped away. Hence, the TiN-capped Co/Si system has induced a ripple-like surface of Co silicide. Besides, the formed Co silicide has been able to endure thermal shock prior the pinhole formation for higher number of pulses. For the TiN/Co/Si system with PAI, the crack that caused by the thermal shock were observed for the 50 pulses of LTA at 0.2 J/cm² whereas it has yet to be observed for the same annealing condition for the system without PAI.

The role of PAI in the capped Co/Si system has caused earlier silicidation. In the Ti/Co/Si system, an explosive crystallization for a single-pulsed LTA at 0.2 J/cm^2 has taken place. However, a mild interdiffusion and intermix of Co and Si atoms was observed in the TiN/Co/Si system without causing explosive crystallization. The explosive crystallization in laser-annealed Co silicide has given rise to the formation of bi-layered structures, i.e., coarse-grained polycrystalline and textured microstructure. In addition, a slightly thicker silicide has formed for the PAI samples compared to that of non-PAI samples. This is due to more heat has been trapped in amorphous Si, promoting the silicidation. When a higher fluence is used, the melt front has exceeded the PAI layer where liquid phase epitaxy regrowth has taken place. Based on the layered structures implemented and the experimental results, the study of the effect of the PAI layer on the silicide formation using LTA does not show any significant advantage. Hence, PAI is not an essential factor for the laser-annealed silicidation.

Single-pulsed LTA at high fluence has sacrificed the formation of thin silicide. CSC phenomenon was observed for the laser-annealed samples with high fluence. From the study of single-pulsed laser annealing in the Ti/Co/Si and TiN/Co/Si system, the CoTi silicide and Co silicide tend to grow along the (111) direction of the Si substrate due to their lowest interface energy. Besides, the twinning defects that resemble stems and branches have formed during the crystallization of molten phase. The adoption of multiple-pulsed LTA at low fluence not only can enhance the interdiffusion and intermix of Co and Si atoms, but also can prevent the rough silicide/Si interface and suppress the twinning defects, resulted by CSC. A single-pulsed LTA at low fluence has

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shown non-melting phenomenon in the capped system without PAI. Nevertheless, melting might have taken place during the subsequent pulses of annealing. This might be attributed to the decrease of surface reflectivity due to the increase of laser-annealed temperature and the change of surface morphology.

For the study of Co/Si system without capping layer, the native oxide on the surface of the Co/Si sample does not hinder the silicidation during LTA. The performance of laser-induced silicidation on thicker Co (13 nm) cannot be produced for thinner Co (8 nm) system, which might be due to less amount of the as-deposited Co. More laser pulses is needed in order to further reduce the sheet resistance of Co silicide in the Co/Si system.

The multiple-pulsed laser annealing at 0.3 J/cm^2 has shown the formation of Co silicide on patterned wafers. A nucleation site where an epitaxy Co silicide has grown was observed in the amorphous Co silicide after LTA. The mixed phases of Co silicide might have contributed to a high sheet resistance. On the other hand, the thin silicide and sharp silicide/substrate interface have contributed to low leakage current.

10.2 Recommendations

The effect of metal impurity can be incorporated into the study of laser-annealed silicidation. For example the elements that are miscible with CoSi_2 are Ni and Au whereas the elements that are insoluble in CoSi_2 are Cu, Ta, W, Pt, Pd and others [88]. These elements can be used to study the influence of impurity in changing the thermodynamics and kinetic growths of silicide through LTA.

A thin layer of capping should be used so that the heat propagated down to the underneath Co layer can be enhanced [99]. As it has been discussed in Section 7.3, the thick capping layer has reduced the heat absorption compared to the Ti-capped Co/Si system for the same annealing condition. However, if too thin of capping layer were used, the ripple periodicity of the surface wave would decrease. In other words, more ripple-like surface will be resulted since the restoring force of the capping layer has decreased with the decreasing of capping layer thickness [100]. Therefore, a compromise between the heat absorption and the ripple-like surface must be made.

In order to reduce the laser-induced ripple-like surface on the Co silicide, a capping layer with high melting temperature but lower thermal expansion coefficient should be used. The alternative choice of capping layer such as HfN and Si_3N_4 can be used to reduce the thermal expansion mismatch between the capping layer and the Co/Si film stacks. The thermal expansion coefficients for HfN and Si_3N_4 are $6.9 \times 10^{-6}/^\circ\text{C}$ and $3 \times 10^{-6}/^\circ\text{C}$, respectively.

The study of laser-annealed silicide can be extended to the investigation of the challenging integration issues which have been discussed in Section 9.3. The mechanisms of causing the reaction between the STI regions and Co layer, delamination of Co silicate on the STI regions and the formation of nanostructures Co silicate (i.e., Co silicate clusters) can be further explored.

Despite the localized silicidation by LTA without heating the entire wafer, phenomena such as the formation of SiO_x in the active area near STI and de-lamination of Co silicate from the STI surface have taken place. This might be due to the pattern density change and the inhomogenous thermal properties across the localized region. It was reported that the exposure window of LTA

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can be expanded by depositing a phase switch layer on top of the transistor [8]. Through this method, the junction/silicide in different regions can be activated uniformly without any pattern damage. Therefore, it is suggested that a phase switch layer can be used during pulsed laser-annealed silicidation in future in order to improve the uniformity of silicide annealing. Besides, a good silicide can be formed if a second RTA at low temperature is carried out [41]. This is because the metastable phase of the silicide after LTA can be easily transformed into a final silicide phase with low resistivity.

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Appendix I

Simulations of implant conditions by Monte Carlo

Appendix II

Crystallographic planes extracted from Powder Diffraction File (PDF)

The 2-theta data were obtained based on $\text{CuK}\alpha_1$ and its Lambda is 1.54056 Å.

CoSi₂

{hkl}	2 theta	Intensity	d _{hkl}
{111}	28.815	90	3.0958
{200}	33.40	2	2.6806
{220}	47.922	100	1.8967
{311}	56.896	23	1.6170
{400}	70.122	17	1.3409
{331}	77.510	11	1.2305
{420}	79.924	2	1.1993
{422}	89.426	25	1.0948
{511}	96.525	6	1.0322
{440}	108.629	10	0.9484
{531}	116.309	5	0.9068
{600}	119.00	2	0.8940
{620}	130.521	13	0.8481
{533}	140.686	3	0.8180

CoSi

{hkl}	2 theta	Intensity	d _{hkl}
{110}	28.419	209	3.1381
{111}	34.991	167	2.5622
{200}	40.625	79	2.2190
{210}	45.674	999	1.9847
{211}	50.321	237	1.8118
{220}	58.803	4	1.5690
{221}	62.760	19	1.4793
{310}	66.580	19	1.4034
{311}	70.292	39	1.3381
{222}	73.921	18	1.2811
{023}	77.484	36	1.2308
{321}	80.998	90	1.1861
{400}	87.939	43	1.1095

Co₂Si

{hkl}	2 theta	Intensity	d_{hkl}
{101}	34.033	30	3.31
{210}	39.308	30	2.88
{111}	41.248	70	2.75
{211}	50.282	50	2.28
{310}	54.100	50	2.13
{021}	56.395	100	2.05
{220}	57.309	70	2.02
{301}	57.937	100	2.00
{121}	58.905	100	1.97
{002}	62.396	100	1.87
{311}	63.147	50	1.85
{320}	69.008	100	1.71
{112}	69.472	30	1.70
{410}	70.905	30	1.67
{130}	74.516	30	1.60
{411}	78.559	30	1.53
{230}	81.098	30	1.49
{420}	84.548	50	1.44
{312}	87.093	50	1.40
{222}	89.906	70	1.37
{510}	90.495	30	1.36
{331}	99.409	30	1.27
{322}	100.487	70	1.26
{412}	102.048	30	1.24
{140}	106.363	70	1.21
{113}	108.976	30	1.19
{600}	109.656	50	1.18
{521}	111.768	50	1.17
{240}	113.241	30	1.16
{610}	114.458	50	1.15
{431}	115.396	30	1.14
{422}	116.357	50	1.14
{241}	121.538	100	1.11
{611}	123.234	100	1.10
{123}	123.622	50	1.09
{313}	128.377	30	1.07
{341}	135.121	30	1.04
{531}	139.640	70	1.03
{621}	141.505	70	1.02
{142}	144.524	70	1.01
{602}	151.231	70	1.00

TiN

{hkl}	2 theta	Intensity	d _{hkl}
{111}	36.663	72	2.4491
{200}	42.597	100	2.1207
{220}	61.814	45	1.4996
{311}	74.070	19	1.2789
{222}	77.964	12	1.2244
{400}	93.172	5	1.0604
{331}	104.677	6	0.9730
{420}	108.611	14	0.9485
{422}	125.678	12	0.8658
{511}	141.320	7	0.8164

Si

{hkl}	2 theta	Intensity	d _{hkl}
{100}	27.074	999	3.2909
{002}	28.452	562	3.1345
{101}	30.658	604	2.9138
{102}	39.679	288	2.2697
{110}	47.835	604	1.9000
{103}	51.782	592	1.7640
{200}	55.827	88	1.6454
{112}	56.600	330	1.6248
{201}	57.894	69	1.5915
{202}	63.838	53	1.4569
{104}	65.966	1	1.4149
{203}	73.147	165	1.2927
{210}	76.529	109	1.2438
{211}	78.301	45	1.2200
{105}	82.211	106	1.1716
{212}	83.560	39	1.1561
{204}	85.495	1	1.1348
{300}	89.209	63	1.0969

TiCoSi

{hkl}	2 theta	Intensity	d _{hkl}
{210}	48.40	50	2.363
{112}	48.818	100	2.344
{202}	49.954	80	2.294
{211}	51.342	100	2.236
{103}	53.103	50	2.167
{013}	58.938	80	1.969
{113}	62.396	50	1.870
{302}	66.914	20	1.757
{004}	67.966	20	1.733
{123}	86.707	20	1.411
{214}	87.717	20	1.398
{314}	102.162	20	1.245

Appendix III

EDX results of a Co/Si system without PAI after a single-pulsed LTA at 0.7 J/cm².

The EDX results shown on pages V and VI is summarized as below:

Location	Element detected by EDX
1	Co, Si
2	Si

No Co was detected at location 2 as compared to that in location 1. The Cu signal collection was inherently originated from sample holder.

EDX result of location 1

EDX result of location 2

Appendix IV

List of Publication

F. L. Chow, K. L. Pey, P. S. Lee, C. H. Tung, X.C. Wang, G. C. Lim, Y. F. Chong,
“Silicide formation from laser thermal processing of Ti/Co bilayers”, *Electrochem.
and Solid-State Lett.* 7 (10), G213-G215 (2004).