STUDY ON THE FORMATION OF SILICIDE PHASE BY
DEPOSITION ERBIUM ON (001)Si

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SUMMARY

Rare earth (RE) disilicides have been identified as ideal candidates for forming heteroepitaxial electronic structure, due to low Schottky barrier height (SBH), low formation temperatures and epitaxy of silicide layer. Among all of the RE silicides, erbium silicide is considered as the most promising material for ohmic or rectifying contacts for two main reasons. First, from an electrical point of view, erbium silicide exhibits a low SBH on n-type Si (\( \Phi_B = 0.28 \text{eV} \)). Second, from a metallurgical point of view, erbium silicide layer can be epitaxially grown on silicon with a high crystallographic quality due to good lattice match between (0001)ErSi\(_2\) and (001) or (111)Si. Moreover, the manufacturing process is compatible with the silicon technology. However, many process-integration issues remain to be resolved in order to realize the proposed device applications of erbium silicides. Two of the crucial issues are the oxygen contamination due to the fast reaction between oxygen and erbium and the pits and pinholes developing on the erbium silicide film surface.

The main objective of this thesis is to investigate the effects of oxygen in the erbium silicidation process. The erbium silicide was grown by the conventional method employing sputtering deposition of Er followed by the rapid thermal annealing (RTA) process to initiate the solid state reaction to form ErSi\(_2\). Two types of ErSi\(_2\) samples were prepared by using different base pressures in the sputtering deposition, which resulted in different oxygen content in the samples. Analyzing the difference of the structures and compositions between the two samples with different oxygen content revealed that the formation of ErSi\(_2\) is influenced both by the presence of oxygen in as-deposited Er (incorporated during sputtering deposition) and by the attack of the residual oxygen in the N\(_2\) ambient during the annealing process.
A possible solution to the oxygen contamination is to deposit a Ti film as a capping layer after the sputtering deposition of Er film. It is found in this work that the Ti capping layer has a beneficial influence on the erbium silicide films. The Ti capping layer helps to broaden temperature range for the formation of ErSi$_2$. The capping layer also improves the film quality. This beneficial effect of Ti capping is attributed to the suppressed incorporation of the oxygen from the annealing ambient to the Er film during the RTA process as well as the oxygen-gettering ability of Ti due to its chemical activity.
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NOMENCLATURE

ABBREVIATIONS

2D Two Dimension
CCD Charge-Coupled Device
CMOS Complementary Metal Oxide Semiconductor
DC Direct Current
DHF Diluted Hydrofluoric Acid
FESEM Field Emission SEM
FWHM Full Width at Half Maximum
GADDS General Area Detector Diffraction System
GI Glancing Incidence
HRTEM High Resolution Transmission Electron Microscopy
IBS Ion Beam Synthesis
IC Integrated Circuit
IR Infrared
MBE Molecular Beam Epitaxy
RBS Rutherford Backscattering Spectroscopy
RCA Radio Corporation of America
RE Rare Earth
RTA Rapid Thermal Annealing
SAED Selected Area Electron Diffraction
<table>
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<tr>
<td>SALICIDE</td>
<td>Self-Aligned Silicide process</td>
</tr>
<tr>
<td>SBH</td>
<td>Schottky Barrier Height</td>
</tr>
<tr>
<td>SBTT</td>
<td>Schottky Barrier Tunnel Transistor</td>
</tr>
<tr>
<td>SC</td>
<td>Standard Cleaning</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XTEM</td>
<td>Cross-section TEM</td>
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**NOTATIONS**

- $\lambda$ : Wavelength
- $\theta$ : Angle
- $d$ : Distance between the lattice planes
Chapter 1

Introduction

1.1 Background

Silicides have been widely used in the integrated circuit (IC) technology due to their high thermal stability, low electrical resistivity and the ability to form reliable electrical contacts on silicon substrates in a self-aligning manner. Silicides are typically used as local contact materials on source, drain and gate regions of complementary metal oxide semiconductor (CMOS) devices to reduce the resistance of the devices [1] and to increase the switching speed for the device operation [2,3]. Silicides are also used for Schottky diodes in bipolar transistors [4] and in infrared (IR) image sensors [5].

Silicide thin films can be formed on a silicon substrate by either a solid state reaction between a metal and Si or by co-depositing the metal and Si. The solid state reaction method is used in a SALICIDE process (self-aligned silicide process), whereas the co-deposition method is used in a polycide process [6]. A typical SALICIDE process is illustrated in Fig. 1.1. The gate and the source/drain junctions are fabricated on a Si wafer; see Fig. 1.1 (a). The patterned wafer is subsequently covered by a blanket metal film using physical vapor deposition (usually sputtering); see Fig. 1.1 (b). The metallized wafers are then subject to thermal annealing process
to form silicides at the exposed Si region; see Fig. 1.1 (c). Finally, a wet etch selectively removes the remaining unreacted metal; see Fig. 1.1 (d).

**Fig. 1.1** Schematic illustrations of the SALICIDE process: (a) the fabrication of the gates, sources, and drains; (b) the deposition of a blanket metal film on the wafer; (c) the thermal annealing process to form silicide on top of the gates, sources, and drains; and (d) selective etch to remove the unreacted metals.
1.2 Introduction to rare earth silicides

The importance of metal silicides to the semiconductor industry has led to the extensive research of the reaction kinetics in various metal/silicon systems. The systems reported in the literature include transition metal silicides such as CrSi$_2$ [7-9] and FeSi$_2$ [10, 11], refractory metal silicides such as WSi$_2$ [12], TaSi$_2$ [13] and MoSi$_2$ [14] and near-noble metal silicides such as TiSi$_2$ [15], CoSi$_2$ [16] and NiSi$_2$ [17, 18].

<table>
<thead>
<tr>
<th>Parameter (units) or property</th>
<th>Rare earth metal (Eu, Gd, Dy, Er…)</th>
<th>Refractory metal (W, Mo, V, Ta…)</th>
<th>Near-noble metal (Ni, Pd, Pt, Co…)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First phase formed</td>
<td>MSi$_2$</td>
<td>MSi$_2$</td>
<td>M$_2$Si</td>
</tr>
<tr>
<td>Formation temperature (°C)</td>
<td>≈350</td>
<td>≈600</td>
<td>≈200</td>
</tr>
<tr>
<td>Grow rate</td>
<td>N/A</td>
<td>x≈t</td>
<td>x$^2$≈t</td>
</tr>
<tr>
<td>Activation energy of growth (eV)</td>
<td>N/A</td>
<td>&gt;2.5</td>
<td>1.1-1.5</td>
</tr>
<tr>
<td>Dominant diffusion species</td>
<td>Si</td>
<td>Si</td>
<td>Metal</td>
</tr>
<tr>
<td>Barrier height to n-type Si (eV)</td>
<td>≈0.40</td>
<td>0.52 - 0.68</td>
<td>0.66 - 0.93</td>
</tr>
<tr>
<td>Resistivity[19, 20]</td>
<td>100 -300</td>
<td>13 -1000</td>
<td>20 -100</td>
</tr>
</tbody>
</table>

Table 1.1 Comparison of the three metal silicide classes (adapted from ref. [21]).

In the microelectronic industry, TiSi$_2$ has been widely used until the technology nodes reach 0.25 µm, and it is replaced by CoSi$_2$, which will be obsolete when the technology nodes are up to 90 nm [22]. The leading candidate to replace CoSi$_2$ for the 65 nm node is NiSi [23]. On the other hand, the silicide material for technology nodes
beyond 65 nm is still an open question, and this has led to intensive searches for new contact materials recently. It was the pioneering work of Baglin and his co-workers [20] that directed the attention of the community to the peculiar properties of rare earth (RE) metal overlayers on Si. They found that thin films of the RE elements Y, Tb and Er could react easily with (111)Si and (001)Si substrates at temperatures as low as 300 °C to form silicides of the type RESi_{2-x}. The value of x is generally between 1.6 and 1.7 [24]. The mechanism of the RE silicides formation is nucleation [25], and the special composition of the RE silicides is caused by silicon deficient. Besides the low formation temperature by nucleation, the RE silicides can also grow epitaxially on (111)Si substrate [26] with low lattice mismatch strain between the silicides and the substrate. The key advantage of the RE silicides over the other types of silicides is that the contacts between the RE silicides and Si exhibit extremely low Schottky barrier height (SBH): 0.3-0.4 eV for n-Si; 0.7-0.8 eV for p-Si [21, 27]. Besides the low SBH, the RE disilicides are also found to be good electrical and thermal conductors. The good properties of the RE silicides in SBH and electrical resistance facilitate the use of the silicides as low resistance ohmic contacts in metallic-based transistors [19, 25, 26, 28-31] and tunable infrared detectors [29, 32].

In addition to the conventional applications of silicides, it was demonstrated recently that a number of RE silicides with the AlB₂ (hexagonal) crystal structure can self-assemble into one-dimensional nanostructures during the epitaxial growth on (111)Si and (001)Si [33-37]. The RE silicides nanowires may have applications in small-scale interconnects [38] and conductors for defect-tolerant nanocircuits [39].
The nanowires can also be adopted as or as a template for further nanofabrication.

### 1.3 Erbium silicides

Among all of the RE silicides, erbium silicide is considered as the most promising candidate for making ohmic or rectifying contacts or low-resistance interconnects in the microelectronic technology for two reasons. First, from an electrical point of view, erbium silicide exhibits an extremely low SBH on n-type Si ($\Phi_B=0.28$eV) [26, 40, 41]. Second, from a metallurgical point of view, erbium silicide layer can be epitaxially grown on silicon with a high crystallographic quality due to good lattice match between (0001) ErSi$_2$ and (001) or (111) Si. Therefore, the material can be used to fabricate interesting novel devices, such as Schottky source/drain in n-MOSFETs [42, 43], gate material in p-channel MESFETS [31], n-type Schottky barrier tunnel transistors (SBTTs) [44], tunable internal photoemission sensors [32], infrared detectors [45] and ohmic contacts. Moreover, the manufacturing process is compatible with the silicon technology.

Although erbium silicides have been investigated rather extensively for infrared detector applications [45, 46], many materials and process-integration issues remain to be resolved in order to realize the proposed device applications. Two of the crucial issues are the instability of the contacts under environmental influences and the poor surface morphology of the silicide thin films. Erbium silicides react readily with gaseous O$_2$. This is a problem in practical applications since the oxidation degrades
the properties of the silicide films. The morphology problem happens during the annealing of the Er film-Si substrate system. The purpose of the process is to initiate the silicide reaction, while the process often leads to rough films with pits and pinholes [20, 47, 48]. The pits and pinholes have a detrimental effect on the electrical performance of the system. Improvements of the thin film morphologies have been achieved by rapid annealing methods [49, 50] and more recently by novel growth techniques such as co-deposition of erbium and Si [51, 52], ultra high vacuum molecular beam epitaxy (MBE) [53], intermediate template layers [54] and ion beam synthesis (IBS) [55, 56].

In spite of the remarkable process, the existing experimental works on erbium silicides were mainly devoted to epitaxial silicide films on (111)Si [32, 43, 57, 58]. The epitaxial growth of ErSi$_2$ on (111)Si substrates is found to be straightforward because both the (111) plane of Si and the (0001) plane of ErSi$_2$ are three-fold symmetry, and the lattice mismatch between the two materials on these two planes is only -1.1% [59]. The epitaxial growth of ErSi$_2$ on (111)Si surface is generally conducted by the MBE method or by electron gun deposition of the metal on precleaned silicon surfaces in an ultra high vacuum (UHV) environment, followed by in-situ heating. Although these methods can produce high quality epitaxial ErSi$_2$ films, they have some fundamental drawbacks in terms of their implementation in the industry: the MBE method is incompatible with mass-production due to its low throughput, while the co-deposition method lacks the self-aligning ability, the most desirable feature for silicide process. Therefore, for technological applications, it is
crucial to adopt conventional techniques such as sputtering deposition followed by rapid thermal annealing (RTA) treatment to grow the erbium silicide. It is also necessary to use the (001)Si substrates, instead of the (111) ones, in order to be compatible with the CMOS technology.

1.4 Objectives and outline

It is known that erbium is highly reactive with oxygen even at room temperature, and the presence of oxygen has been demonstrated to affect erbium silicidation process and film morphology. The objectives of this thesis study are (1) to identify the suitable conditions for the Er/Si solid state reaction by examining the phases, microstructures and diffusion profiles of the element, (2) to investigate the influence of oxygen ambient on erbium disilicidation process and (3) to develop an effective method to minimize oxygen contamination in the Er/Si system. The erbium silicide was grown by the convention method employing sputtering deposition of Er followed by the RTA process to initiate the solid state reaction to form ErSi$_2$. Two types of the ErSi$_2$ samples were prepared by using different base pressures in the sputtering deposition, which resulted in different oxygen content in the samples. The two types of samples were then analyzed by X-Ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM) to determine the crystal structures and compositions in the samples. Analyzing the difference of the
structures and compositions between the two samples with different oxygen content revealed the effects of the oxygen during the erbium silicidation. The ErSi₂ formation is found to be sensitive to the presence of oxygen. Oxygen incorporation (or contamination) may originate from different sources such as the RTA process and the Er sputtering process. A possible solution to the oxygen contamination is proposed to deposit a Ti film as a capping layer after the sputtering deposition of Er film. The Ti capping layer has been found to have a beneficial influence on the erbium silicide films mainly on two aspects. First, the capping layer helps to broaden temperature range for the formation of ErSi₂. Second, the capping layer also improves the film quality. This beneficial effect of Ti capping is attributed to the suppressed incorporation of the oxygen from the annealing ambient to the Er film during the RTA process as well as the oxygen-gettering ability of Ti due to its chemical activity.

The thesis is outlined as follows. Chapter 2 reviews the background and the relevant literature of the growth and the characterization of ErSi₂. Chapter 3 describes the experimental procedure adopted in this thesis and the characterization techniques used to analyze the structures and the compositions of the system, which includes SEM, XRD, TEM, XPS, and SIMS. Chapter 4 presents the characterization results of ErSi₂ prepared under different base pressures. By the similar characterization techniques, Chap. 5 examines the case where the ErSi₂ films are covered by a Ti capping layer. The thesis concludes with a summary in Chap. 6.
References:


Chapter 1 Introduction


Chapter 2

Literature Review

In this chapter, we will give a brief review of the previous work on erbium silicide and other RE silicides. Two crystal structures of erbium disilicide epitaxially grown on (001)Si will be presented at first. Surface morphology of erbium silicides and possible mechanisms for pinholes formation will be discussed afterwards. In addition to the previous studies about growth of RE silicides on silicon, proposed models describing reaction mechanisms in RE metal-silicon system will be also summarized.

2.1 Crystal structure of erbium disilicides

ErSi$_2$ thin layers can be grown epitaxially on (001)Si in two crystalline phases: one is the hexagonal AlB$_2$ type crystalline structure, and the other one is the tetragonal ThSi$_2$ type structure. Whether the AlB$_2$ or the ThSi$_2$ structure will develop on the (001)Si substrate is determined by several factors, including the growth method, the growth temperature, the stoichiometry of the layer, and, to a lesser degree, the stress developed in the layer during the growth process [1, 36-38].
2.1.1 Hexagonal AlB$_2$ type crystal structure

Fig. 2.1 Schematic of the AlB$_2$ structure: (a) spatial model; (b) top view of ErSi$_2$ grown on the on-axis of (001)Si.

| Epitaxial Relationship for \{1\overline{1}00\}ErSi$_2$ // (001)Si |
|-------------------------|-------------------------|-------------------------|
| $[1\overline{1}2\ 0]$ ErSi$_2$ // $[01\overline{1}]$ Si       | $[0\ 0\ 0\ 1]$ ErSi$_2$ // $[01\overline{1}]$ Si |
| Lattice Mismatch       | Lattice Mismatch       |
| -1.1%                  | 6.4%                   |

Table 2.1 The epitaxial relationship and lattice mismatches for \{1\overline{1}00\}ErSi$_2$ // (001)Si.
The AlB$_2$ structure of erbium silicides is a defective AlB$_2$ structure [2] with the space group P6/mmm. As shown in Fig. 2.1 (a), the defective AlB$_2$ structure consists of alternate (hexagonal) Er and Si planes that are parallel to the sample surface or interface. One out of six Si atoms is missing in the silicon planes relative to the ideal AlB$_2$ structure, leading to the composition Er:Si=1:1.7 [2, 3, 39]. Vacancy ordering is thought to take place in the bulk material.

The AlB$_2$ structure of erbium silicides can grow epitaxially on (111) and (001) plane of Si. In the former case, it is the (0001) plane of erbium silicide that grows on (111)Si. The lattice mismatch between these two planes is -1.22 % at room temperature [2]. Thus, under ideal conditions, the c plane of the erbium silicide layers would match up to the three-fold symmetric (111) plane of Si [3, 4]. In the second case, the a plane of the AlB$_2$ structure of erbium silicides grows on (001)Si with the a and b axis of AlB$_2$ aligning with the [100] and [010] directions of Si, respectively. Lattice parameters of ErSi$_2$ [5] (a$_\text{hex}$=3.798 Å and c$_\text{hex}$=4.088 Å) are close to the $\frac{1}{2}$a <110> in Si [6] (=3.840 Å). Therefore, the rectangular {1100} side planes of the hexagonal ErSi$_2$ prism, which include the a and c axes in the plane, are expected to grow epitaxially on the (001)Si surface including two <110> directions in the plane (four-fold rotational symmetry), in contrast to the hexagonal (0001) basal plane in the (111)Si surface including three <110> directions (three-fold rotational symmetry).

Lee et al [7, 8] showed the double domains of ErSi$_2$ films by studying the epitaxial growth of erbium silicide on (001)Si through a solid phase reaction. The double domains come from the fact that the a plane of erbium silicides in the unit cell
is a rectangular in contrast to the (001) plane of Si in the unit cell. Therefore, when the a plane of erbium silicides grows on the (001) plane of Si epitaxially, there are two ways to match the two planes. In particular, the long axis (the c-axis) of the rectangular a plane can align with the [100] or the [010] directions of the (001)Si surface, as shown in Fig. 2.1 (b). Table 2.1 summarizes the epitaxial relationship and lattice mismatches for this case.

**2.1.2 Tetragonal ThSi₂ type crystal structure**

![Spatial model for the ThSi₂ structure.](image)

**Fig. 2.2** Spatial model for the ThSi₂ structure.
The tetragonal ThSi$_2$ structure has been reported to grow epitaxially on (001) Si [9]. Figure 2.2 shows the spatial model for the ThSi$_2$ structure of ErSi$_2$. For the ThSi$_2$ phase on (001)Si, the epitaxial relationships are $a//Si[011]$, $b//Si[01\ 1]$ and $c//Si[100]$, where $a$, $b$ and $c$ are the unit vectors of ThSi$_2$, respectively.

Kaltsas et al [9] assumed that the ThSi$_2$ structure can be derived from the AlB$_2$ by introduction of shear planes (parallel to the $(10\ 10)_{\text{hex}}$ planes) with a shear vector $(b_{\text{hex}} + c_{\text{hex}})/2$ and a period of $a_{\text{hex}}/\sqrt{3}$. Small changes of the lattice parameters are required to maintain the tetragonality. As a consequence, the lattice parameters of the two structures are related as follows:

\[
\begin{align*}
a &= b \approx (a_{\text{hex}} + c_{\text{hex}})/2 \\
c &= 2a_{\text{hex}}/\sqrt{3}
\end{align*}
\] (2.1) (2.2)

Epitaxial erbium silicide films on (001)Si using different growth methods has been studied by Travlos et al [1]. It was found that a layer of Er metal can react with the silicon substrate to form the hexagonal ErSi$_{2-x}$ phase in the temperature ranging from 450 to 800 °C. The tetragonal phase, in contrast, appears at reaction temperatures of 870 °C or higher. Growth of ErSi$_{2-x}$ by the deposition of Er/Si bilayers or by the co-deposition of Er and Si results in the formation of the tetragonal phase at 800 °C.

The work by Cai et al [10] suggests that whether the AlB$_2$ or the ThSi$_2$ structure forms on (001) Si may be affected by the nanostructures developing during the early stage of the growth process. When a few monolayers of erbium are deposited on (001)Si, the erbium film will develop into nanowires. On the surface between nanowires, new $(5 \times 2)$ reconstruction are observed which may have the
crystallographic orientation relationship of AlB$_2$ structure grown on (001)Si surface. With increasing Er coverage, nanowires assemble to form rectangular islands. Then Er silicide begins to crystallize into ThSi$_2$ structure and grows into square islands.

2.2 Surface morphology of erbium silicides

The surface morphology of the silicide is typically dominated by pits with regular shape. The pits generally exhibit the symmetry of the underlying Si substrate. The size of the pits is few micrometers and the depth can be two or three times the total silicide thickness. In other words, the pits on the erbium silicides surface can penetrate into the Si substrate. Meanwhile, the pits forming on (001)Si have a square or a rectangular base; in contrast, the base of the pits is triangular when forming on (111)Si. The result suggests that the pits are related to the crystalline nature and orientation of the Si substrate [11]. Those pits may have deleterious effects on both electrical and optical properties of the silicide films [12]. Several methods, such as capping [13, 27], intermixing [14] and co-evaporation [1], have been used to be attempted to remove pinholes on the surface. These methods, however, are not feasible from a manufacturing point of view.

It is important to note that similar phenomena have been observed in many other rare earth silicide systems such as DySi$_2$ [15] and YSi$_2$ [16]. Several mechanisms have been proposed and they can be generally classified into four types.

1) There is nonuniform contaminant barrier at the interface between metal and
silicon. The barrier prevents the Si atoms from diffusing to react with metals [17, 18]. The thin contamination barrier may be due to the presence of residual oxide or other contamination species.

2) The surface energy of erbium silicide is higher than that of Si substrate, making it energetically more favorable to expose bare Si by the generation of pinhole in epitaxial Erbium silicide thin films [19].

3) Volmer-Weber growth may result in the formation of pinhole [20-22]. The occurrence of this nucleation controlled reaction, typically taking place nonuniformly, throughout the interface would be expected to leave behind voids in the film, which act as seeds for the formation of pinholes. Once they form, the pinholes become thermodynamically more stable and their removal is nearly impossible [18].

4) Pinholes may form in order to release tensile stress during the erbium silicide formation [20].

Unlike the previous reports, the defects observed in our work have a pyramidal shape with the apex directed away from the substrate. The possible mechanism of such defect formation will be discussed in Chapter 5.
2.3 Previous studies on growth of rare earth silicides on silicon

Application of erbium silicides in microelectronics requires a good understanding of their materials and physics properties and also their growth mechanism. In this section, we will briefly review the previous studies on the growth of RE silicides.

It must be pointed out first that despite the rather extensive works carried out so far, many questions about the growth mechanisms of RE silicides on the Si substrate remain to be answered. For example, several contradictory reports exist in the literature about the growth of thin rare earth silicide layers on single crystal silicon. Thompson et al [11, 23] studied the solid phase reaction of 200 nm thick rare earth layers deposited at 100 °C on (001)Si substrates. They found that the rare earth metal layers reacted with silicon to form disilicides within a narrow temperature range after annealing at 300–350 °C for less than 30 min. From ion backscattering studies, they concluded that the growth of the RE disilicides did not follow the layer-by-layer growth mode. In a similar but slightly different experiment, Hsu et al [24] studied the solid phase reaction of 50 nm thick rare earth layers on (001) and (111)Si substrates and followed by depositing protective layers of Mo and Nb on the erbium film. They then annealed the samples at temperatures ranging from 200 to 600 °C for 15-60 min by conventional furnace, rapid thermal annealing and laser annealing. Their samples were examined by ion backscattering, Auger spectroscopy, X-ray diffraction, and transmission electron microscopy. They reported that although the reaction of the rare
earth layers with silicon started at 200 °C, the disilicide phase did not occur until 600 °C. d’Heurle et al [25] studied the reaction of rare earth layers on (001) and (111)Si at 300-500 °C with ion backscattering and suggested that the formation of RE silicides was dominated by nucleation controlled mechanism [26].

On the other hand, some experiments on the growth of thin rare earth silicides on Si showed that the reaction between rare earth and Si starts at room temperature and proceeds via the layer-by-layer growth mode. Gokhale et al [27] deposited 20 nm Dy metal layers on (001)Si substrates at room temperature and annealed them at 150 and 350 °C for 60 min. Examination of these samples by glancing angle X-ray diffraction and X-ray photoemission spectroscopy revealed that the interaction between Dy and Si was strong even at room temperature, resulting in the formation of a thin Dy₅Si₃ layer at the interface. At higher annealing temperatures a graded interface of DySi₂₋ₓ on an amorphous background was observed. For the formation of Er silicides, Roge et al [28] studied the interaction of Er metal with Si by depositing a few monolayers of Er on (111)Si substrates and annealing at 500 °C for a few minutes. Scanning tunneling microscopy and angle-resolved photoemission measurements showed that the reaction proceeded via the layer-by-layer growth mode up to a few monolayers, forming ErSi₂.

More recently, Shen et al [29] reported experiments on the growth of DySi₂₋ₓ on (111)Si. They studied a 30 nm thick Dy layer deposited on (111)Si at room temperature and capped by an amorphous Si layer of 15 nm. After annealing at 400 °C for 30s, TEM examination of the sample showed that recessed regions were observed
at the silicides/Si interfaces and the thickness of DySi_{2-x} layer in the recessed regions was greater than in the more planar regions. This behavior was interpreted by Shen et al as manifestation of Stranski–Krastanov (layer plus island) type of growth.

Luo and Chen [30] reported experiments on the growth of ErSi_{2-x} and TbSi_{2-x} on (001)Si. They deposited 20 nm of Er and Tb on Si substrates at room temperature followed by a protective layer of 20 nm of Mo. The samples were annealed in N\textsubscript{2} ambient at temperatures in the range of 190-300 °C with the duration varying from 8 to 60 mins. The TEM examination of the annealed samples showed that an amorphous interlayer was present at metal/silicon interface of the as-deposited samples which grew during annealing. At higher annealing temperatures and/or prolonged annealing, crystalline silicide was nucleated at the \textit{a}-interlayer/Si interface, which grew at slower rate than the \textit{a}-interlayer.

Travlos et al [31] studied Dy layers deposited on (001)Si (with substrate temperature kept at 300 °C) for different durations in order to produce DySi_{2-x} layers at several stages of growth. The results of TEM suggested that silicon reacted with Dy with the simultaneous growth of an amorphous interlayer and DySi_{2-x}. Compressive stresses due to volumetric changes during the reaction deformed the produced silicide layer and induced roughness on the DySi_{2-x}/Si and the DySi_{2-x}/amorphous layer interfaces.
2.4 Proposed models describing reaction mechanisms in RE metal - silicon system

In this section, we will discuss various models proposed for the reaction of RE metal layers with silicon and the morphology of the resulting silicide layers.

The first of these models (Fig. 2.3) is based on the assumption that RE silicide layers grow only after the nucleation of the silicide at the RE/Si interface [11]. In this model, it is proposed that RE silicides form rapidly within a narrow temperature window (e.g. 325-400 °C for erbium disilicides) through nucleation process and are stable up to 900 °C, with a very uniform and sharp interface. Both the ion backscattering and optical microscope studies indicate that the disilicide nucleated in a few spots and then grew as isolated islands, as shown in Fig. 2.3.

![Fig. 2.3 Illustrations of erbium disilicide formation based on the nucleation growth assumption: (a) as deposited; (b) disilicide nucleated; and (c) pits formed. (adapted from ref. [20])](image-url)
The second model [2, 33, 34] invokes the presence of an interfacial contaminant barrier between Si and deposited Er, which prevents silicide growth until it has been removed, as illustrated in Fig. 2.4. The thin barrier layer is expected to have a high activation energy for dissolution, while the silicide has a relative low activation energy. Thus, at the stage of annealing, the rate of barrier removal would be much lower than the rate of silicide formation. Pits would form at holes or thin spots in the barrier, as the Si migrates up through the hole and laterally through the Er layer to form the silicide. As the rest of the barrier is dispersed, silicide formation takes place across the surface. Since the relative rate of silicide formation is much faster than the barrier dissolution, the resulting surface is rough and pitted.

**Fig. 2.4** Schematics of the Er/Si reaction on the basis of the presence of an interfacial contaminant barrier (a) an interfacial thin barrier which has a high activation energy for dissolution; (b) pits beginning to form at pinholes in the barrier; and (c) final surface after annealing.
Figure 2.5 schematically illustrates the third model proposed by Luo et al [30] and Chen et al [35]. According to this model, when Si reacts with the RE material, an amorphous layer of RESi$_{2-x}$ forms. Subsequently, the amorphous layer that is in contact with the Si substrate will develop into epitaxial RESi$_{2-x}$ during annealing process. Chen et al suggested that the growth of epitaxial ErSi$_{2-x}$ regions competed with that of the amorphous interlayer. The epitaxial ErSi$_{2-x}$ regions also acted as a diffusion barrier for the further inter-diffusion of Er and Si. The competing growth mechanism led to the formation of the uneven interface. The model also predicts that the rough interface with high total interface energy is unstable; as a consequence, the interface may evolve into pinholes when annealed at high temperatures.

Recently, Travlos et al [31] proposed a mechanism for RE silicide growth based on their study of Dy layers deposited on (001)Si substrates, as shown in Fig. 2.6. The major differences between this model and those discussed above are the severe deformation and lifting off of the silicide layer. According to this model, such severe deformation and lifting off the substrate is due to stresses associated with volumetric changes during silicide formation. This severe deformation results in non-uniform diffusion of Si in the $a$-interlayer because Si is preferentially removed from the points where the silicide is in contact with the substrate. The non-uniform diffusion in turn induces roughness at the surface and interface of the silicide layer.
Fig. 2.5 Schematics of sequence of simultaneous growth of the $a$-interlayer and erbium silicide formation found in this model (a) the formation of $a$-interlayer in as-deposited samples; (b) the stage at which isolated epitaxial ErSi$_{2-x}$ regions begin to form at the $a$-interlayer/c-Si interface; (c) the recessed amorphous regions beginning to form between isolated epitaxial ErSi$_{2-x}$ regions; and (d) diffusing of the Si and Er atoms through the openings, leaving behind recessed amorphous regions, eventually the growth of $a$-interlayer slowing down in the diffusion-controlled stage with increased diffusion distance, and the ErSi$_{2-x}$ regions growing to form a continuous thin film.
Fig. 2.6 Schematics of the proposed growth model (a) at room temperature, RE metal and Si form a thin continuous $a$-interlayer; (b) at the initial stages of annealing, silicon from the substrate diffuses through the $a$-interlayer into the RE metal increasing the thickness of this amorphous layer; (c) the RESi$_2$ forms at some region and the whole epi-layer becomes deformed and lifts off in part from the substrate due to stresses associated with volumetric changes during silicide formation. Meanwhile, the Si atoms can only continue to diffuse at the points where the silicide layer is still in contact with the substrate; and (d) finally, when the whole RE metal has been transformed into RESi$_{2-x}$, compressive stresses diminish and the silicide layer relaxes back onto the silicon substrate.
References:


Chapter 3

Fabrication and Characterization Method

In this chapter, the experimental procedure of erbium silicide films fabrication on (001)Si are described in Sec. 3.1. In addition, the characterization methods with respect to the mechanical and structural properties of ErSi$_2$ are presented. The characterization techniques include X-Ray Diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM). They are briefly discussed in Sec. 3.2.

3.1 Erbium silicide sample preparation

In this work, erbium silicide films on (001) silicon were fabricated by three main steps: standard cleaning procedure, sputtering deposition, and RTA treatment. The three steps are briefly discussed in the following three subsections.

3.1.1 Wafer cleaning

Prior to erbium deposition, the Si substrate was chemically cleaned to remove impurities and particles from the substrate surface. The substrates used for deposition are n-type phosphorous-doped and p-type boron-doped silicon. The resistivity of the wafer was around 10$^{-15}$ $\Omega$cm for both types of Si substrates. The standard substrates were
cleaned by the RCA (Radio Corporation of America) cleaning procedure [1]. The RCA cleaning procedure was developed in 1960 and became the common cleaning method in the industry. The substrate cleaning process is illustrated in Fig. 3.1. First, the conventional chemical cleaning using the SC-1 (standard cleaning) solution (NH₄OH:H₂O₂:H₂O =1:1:5 for 10 minutes at 80-90 °C) was performed to remove organic contamination and particles by oxidation. Subsequently, the SC-2 solution (HCl:H₂O₂:H₂O =1:1:6 for 10 minutes at 80-90 °C) was used to desorb metal contamination by forming a soluble complex. Finally, the substrate was dipped into diluted hydrofluoric acid (DHF) (HF:H₂O =1:5) for 2 minutes to remove the native or chemical oxide.

Fig. 3.1 Cleaning process of Si substrate.
3.1.2 Film deposition

(a) Sputtering system

Denton (Discovery-18) sputtering system was used for Er thin film deposition. In this sputtering system, all of the cathodes are arranged to point to the same area on the substrate holder. The substrate holder provides continuous substrate exposure to cathodes during sputtering, and results in coating uniform film, whose thickness variation is less than 5% [2]. The cathode arrangement is shown in Fig. 3.2. The erbium and titanium targets used in this work were 99.9 at% pure.

Fig. 3.2 Confocal cathodes arrangements in Denton Discovery 18 sputter deposition system.
(b) Deposition rate calibration

Sputtering rate calibration for erbium and titanium were carried out to determine the proper deposition time for intended thickness with a fixed power supply (such as 250 W for Er). The film thickness was measured by surface profiler (ALPHA STEP 500). Figure 3.3 shows the film thickness as a function of deposition time for erbium. The data was fitted by a linear equation using the standard least square method. The linear equation was employed to predict the proper sputtering time for 35 nm erbium.

\[ y = 0.66185x + 6.95098 \]

Fig. 3.3 Film thickness as a function of deposition time for erbium.
(c) Metal film deposition

The cleaned wafers were inserted into the chamber immediately after dipping into DHF and the pressure in the chamber reduced to the range between $5 \times 10^{-7}$ and $4 \times 10^{-6}$ torr. Before the substrate was deposited with the Er material, the target in the deposition system was sputtered for 5 minutes with the shutter closed in order to eliminate contamination layer on the target surfaces.

Figure 3.4 shows the schematic of DC (direct current) plasma sputtering. The charged Ar ions in the Ar plasma acquire enough energy from the voltage difference between the cathode and anode, and hit the cathode (target) surface. The momentum of the Ar ion transfers to the target material through phonon interactions. The result is the ejection of one or more neutral atoms from the target surface. The ejected atoms fly through the plasma (with a small chance of being ionized on the way) and land on the wafer.

Fig. 3.4 Schematic of DC plasma sputtering.
In this work, two kinds of samples were prepared. In the first kind of samples, erbium was sputtered for 42 seconds at 250 W, which resulted in the deposition of 35 nm erbium on (001)Si. In the second kind of samples, titanium was deposited immediately after the deposition of the 35 nm erbium film. The correlative parameters for the deposition of Er and Ti were listed in Table 3.1.

It is known from the previous works that erbium is highly reactive with oxygen and the presence of oxygen has been demonstrated to affect silicidation process and film morphology [3, 4]. Therefore, capping layer was deposited because it can be a protective layer for erbium to minimize oxygen contamination.

<table>
<thead>
<tr>
<th></th>
<th>Er (Erbium)</th>
<th>Ti (Titanium)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Power (W)</td>
<td>250</td>
<td>167</td>
</tr>
<tr>
<td>Sputtering time (s)</td>
<td>42</td>
<td>72</td>
</tr>
</tbody>
</table>

**Table 3.1** Sputtering set up conditions using in the work.

### 3.1.3 Rapid thermal annealing (RTA)

Heat treatment of erbium thin films was carried out in a rapid thermal annealing system (ADDAX 80 system) to promote solid state reaction of the deposited Er and
underlying Si substrate. Solid state reaction between a metal thin film and a silicon wafer is the simplest method to obtain silicides. Heating the metal/Si system will cause it to evolve to a thermodynamically more stable state. RTA is a process which uses lamp heating and water cooling to control the temperatures during the annealing process. The samples were annealed in nitrogen ambient at temperatures ranging from 400 °C to 800 °C for 1 minute. The schematic of RTA equipment is shown in Fig. 3.5.

The RTA process offers a superior means for silicide formation compared with the traditional furnace annealing [5]. Practically, the RTA system has a much better control of the annealing temperature, annealing time and temperature ramping (up and down). The maximum ramping rate on Si wafer is 100 °C without regulation and 80 °C with regulation.

Fig. 3.5 Schematic of rapid thermal annealing system.
3.2 Characterization methods

X-Ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM) were used to characterize the erbium silicide films. These characterization methods are briefly discussed in this section.

3.2.1 X-Ray diffraction (XRD) method

(a) Principle

X-Ray Diffraction characterization was performed on the samples to monitor the phase formation sequence. Figure 3.6 (a) shows the two dimensions model of diffraction of x-ray by thin film. X-ray beam, whose wavelength is $\lambda$, enters into the thin film at the angle of $\theta$, and reflects at each crystal plane, where $d$ is the distance between the planes. The pathways of the X-ray beams reflected two adjacent planes differ in distance by $2dsin\theta$. When this length is equal to an integral multiple of the wavelength of the x-ray, which can be expressed by the relation,

$$2dsin\theta = n\lambda \quad (3.1)$$

reflection intensifies and a peak appears. Equation (3.1) is called Bragg's formula. The schematic drawing of XRD equipment used in this study is shown in Fig. 3.6 (b).
(b) System description

Bruker AXS General Area Detector Diffraction System (GADDS) (as shown in Fig. 3.7) was used in this work. The core of GADDS is a two-dimensional (2D) area detector and a photon-counter device. The speed of data collection with an area detector could be 104 times faster than with a point detector and about 100 times faster than that with a linear position-sensitive detector. More importantly, compared to the one-dimensional diffraction profiles measured with a conventional diffraction system, a 2D image collected by GADDS contains more information such as texture, residual stress, crystal size and percent crystallinity. The disadvantage of Bruker AXS is the reduced resolution of detected intensity.

Three main methods of the X-ray diffraction characterization were employed. The first method is known as glancing incidence (GI) scan, also called the seeman-bohlin geometry. This method is used for the phase identification and it is better for lateral...
resolution rather than depth resolution. By using a glancing angle of incidence (usually at a glancing angle of \( \sim 1^\circ \)), a large area of the thin film sample is analyzed. The second method, Gonio scan, also called Bragg-Brentano scan, is usually for bulk material analysis. Bragg-Brentano X-ray diffraction technique is not an ideal technique for ultra thin films characterization because of the low sensitivity and the interfering effect of the substrate. Due to the thick ErSi\(_2\) deposited and its highly epitaxial nature, Gonio scan can be used to examine the quality of the silicide films. The film crystallinity or epitaxy of the ErSi\(_2\) films was investigated using the rocking curve, the third method, focusing around ErSi\(_2\) (1 \( \bar{1} \)00) diffraction peak. Using this characterization method, the quality and texture of ErSi\(_2\) thin film formed can be predicted and analyzed. In summary, glancing incidence X-ray diffraction spectrometry, Gonio scan and rocking curves were carried out using Bruker AXS, operating at 40 kV and 40 mA with Cu-K\(\alpha\) radiation in this work.

Fig. 3.7 Five major units in a GADDS XRD system: (i) x-ray generator (sealed tube) to produce x-rays; (ii) x-ray optics (monochromator and collimator) to condition the primary x-ray beam; (iii) goniometer and sample stage to establish and maneuver the geometric relationship among primary beam, sample, and detector; (iv) sample alignment and monitor (laser-video) to assist users in positioning the sample into the instrument center and in monitoring the sample state and position; and (v) area detector to intercept and record the scattering x-rays from a sample and to save and display the diffraction pattern into a two-dimensional image frame.
3.2.2 Scanning electron microscopy (SEM)

The surface morphology of erbium silicide thin films was observed by the scanning electron microscopy (SEM). The SEM analysis in this work was performed using a JSM-6700F field emission SEM (FESEM) operating at a maximum voltage of 20 kV. An FESEM incorporates a cold cathode field emission gun, ultra high vacuum, and sophisticated digital technologies for imaging of micro structures. Featuring a conical FE gun and a semi-in-lens objective lens, the system is capable of high resolution imaging as well as high quality real time image display at all scan speeds, enabling observation and recording of superior images even in a bright room.

3.2.3 X-ray photoelectron spectroscopy (XPS)

XPS is one of the most frequently used surface analysis techniques [6, 7]. It offers information on the surface elemental composition, the chemical state of the elements and the electronic interaction between ions in the samples.

XPS measurements were employed to investigate the film composition of ErSi$_2$ and analyze the chemical binding states. All measurements were done using a VG ESCA Lab 220i-XL instrument, which was equipped with a hemispherical energy analyzer and a magnetic immersion lens (XL Lens) to maximize the sensitivity. All spectra were obtained in the constant pass energy mode with pass energy of 10 eV using monochromatic Al K$_\alpha$ source (1486.6 eV) at a photoelectron take-off angle of 90°. The background pressure in the measurement chamber was normally at 1.5×10$^{-8}$ Pa. Qualitative analysis whereby elemental and chemical identification of sample
constituents can be performed by combining the information in the survey spectra with the binding energy tables.

### 3.2.4 Secondary ion mass spectroscopy (SIMS)

SIMS is a surface analytical technique that uses an ion beam to remove small numbers of atoms from outermost atomic layer of a surface. The technique uses a beam of energetic (0.5-20 keV) primary ions to sputter the sample surface, producing ionized secondary particles that are detected using a mass spectrometer. Figure 3.8 illustrates the SIMS method. Many neutral species are formed by the interaction of the beam with the samples, but it is the positive and negative ions that provide meaningful information for SIMS. These charged species, called "secondary ions", are extracted by electric fields and then analyzed to determine the energy and the mass of the ions. The intensity of one particular species can be measured as a function of time. The obtained information can be converted into the results of concentration versus depth.

![Fig. 3.8 Schematic drawing of SIMS system.](image)
3.2.5 Transmission electron microscopy (TEM)

(a) Principle

High resolution TEM (Philips CM 400 TEM) was used to characterize physical thickness, film quality and interface condition in this work. Figure 3.9 shows a schematic diagram of a typical TEM system. The focus lenses change the convergent angle and beam size of the electron beams emitting from the electron gun. The electron beam transmits through a thin regime of the sample, passes the objective lens and projective lens, and finally reaches the fluorescent screen. In addition to displaying the image on the screen, the image can also be captured by the CCD (charge-coupled device) camera and recorded in the system. The electrons interact strongly with lattice by scattering. Thus, the sample has to contain a thin regime in order for the electron to pass through. Required thickness of the thin regime is 5-500 nm at 100 kV. TEM images can have resolution as high as 0.2-0.3 nm when operating at 200 kV.

(b) Sample preparation

A common sequence of preparation techniques for preparing TEM samples is illustrated in Fig. 3.10. The sample needs gluing together (film towards film), ultrasonic disk cutting with diameter 3 mm, followed by polishing, dimpling and ion milling [8]. The sample is completed until there is a thin regime in the center and this transparent material should be less than 50 nm thick.
Stacking curing 30-40 mins
Cut & polish one side Glue to Cu grid
Polish the other side
Dimple
Sample for TEM characterization

**Fig. 3.9** Schematic of TEM system.

**Fig. 3.10** Process steps of preparing samples for TEM characterization.
References:


Chapter 4

The Effects of Oxygen on Erbium Silicidation

Erbium disilicide has received much attention due to its low SBH on n-type Si [1, 2] and its ability to form good epitaxial film on both (111) and (001) silicon substrates [3] as we discussed in Chapter 1. It is also known from the previous work that erbium is highly reactive with oxygen even at room temperature [4, 5] and the presence of oxygen has been demonstrated to affect erbium silicidation process and film morphology [6, 7]. Therefore, it is of high importance to investigate the influence of oxygen incorporation on the formation mechanism of erbium disilicide during erbium silicidation.

This chapter starts with a brief discussion of the design of our experiments where two sets of the samples were prepared with different base pressures in the Er sputtering deposition process. The formation of Er disilicide on both sets of the samples after the RTA process is confirmed by XRD and the details of the results are discussed in Sec. 4.2. Erbium disilicide films formed on both sets of the samples by 500 °C annealing are then compared by means of cross-section TEM, which shows microstructure of the films. Selected area diffraction (SAD) is also applied to determine the orientation relationships between the grown erbium disilicide layer and the (001)Si substrate. This result is illustrated in Sec. 4.3. In order to understand the composition of the film, SIMS is adopted to determine the distribution profile of oxygen in Erbium silicide films formed after RTA of Er/(001)Si at different temperatures. The results indicate that the oxygen incorporation (during Er deposition
and also RTA process) has a significant effect on the ErSi$_2$ film formation. The SIMS analyses and the discussion of the results are presented in Sec. 4.4. Possible mechanism for the incorporation oxygen influence on the formation of erbium disilicide during erbium silicidation is discussed in Sec. 4.5.

### 4.1 Experiment

![35nm Er](image)

**Fig. 4.1** Two sets of the samples prepared with different base pressures: (a) **E1**: $4 \times 10^{-6}$ torr and (b) **E2**: $5 \times 10^{-7}$ torr.

Two sets of the samples were prepared by sputtering 35 nm of Er films on (001)Si substrates with different base pressures (see Fig. 4.1 for details). For the first set of the samples, labeled as **E1**, the base pressure in the deposition chamber was kept at $4 \times 10^{-6}$ torr before erbium deposition. The substrate was kept at room temperature during Er deposition. For the second set of the samples (**E2**), the base pressure was lower than $5 \times 10^{-7}$ torr before Er deposition. Other processing conditions were remained the same. The argon gas flow was turned on during the deposition process to generate Ar ions for sputtering; the gas flow rate was kept at 25 sccm. The pressure in the chamber was about $2 \times 10^{-3}$ torr during the sputtering deposition. The two types of the samples were then subject to RTA treatment at
temperatures ranging from 400 °C to 800 °C to form ErSi$_2$. A pure nitrogen gas was introduced into the RTA chamber to minimize the oxygen partial pressure in the chamber. The silicide films formed were then characterized using XRD, TEM and SIMS techniques.

4.2 XRD results

4.2.1 Phase identification

The phases of Er silicide films formed on the two sets of the samples after the RTA silicidation were examined by XRD. In particular, the Gonio scan and the glancing incidence (GI) scan of XRD were adopted in our investigation. The XRD analyses were carried out using Bruker AXS GmbH 2000 system equipped with a Cu-ka radiation operating at 40 kV and 45 mA.

Gonio (also called standard Bragg-Brentano geometry) scan was performed using a continuous mode with a step size of 0.03°. In the GI mode, the incidence angle was fixed at 1°. Erbium disilicide thin films can be easily detected by the conventional XRD Gonio scan because, typically, the ErSi$_2$ forms epitaxially on (111)Si and (001)Si due to minimum lattice mismatch with certain orientation relationships. However, Gonio scan mode is difficult to determine the crystal structure in very thin films due to the low sensitivity and the interfering effect of the substrate [8]. On the other hand, GI scan is used to probe a thin film sample with a high intensity. Hence it is capable of characterizing multiphase for a material with rather randomly orientated grains in a thin film [8]. Therefore, both Gonio and GI scans can be used to obtain comprehensive information to completely identify the phases in Er/Si films.
4.2.2 XRD results and discussion

Figures 4.2 (a) and 4.2 (b), respectively, plot the Gonio and GI scan results of Sample E1 after RTA silicidation at temperatures ranging from 400 °C to 800 °C. For comparison, the results of as-deposited E1 are also included in the figures.

From the plots, the peak corresponding to Er (002) is observed on the as-deposited sample and it disappears after RTA at 400 °C and above. This suggests that the sputter-deposited Er remains unreacted on the Si surface at room temperature. In addition, for the samples that were RTA annealed at 500 °C, ErSi₂ (1\overline{1}00) and (2\overline{2}00) peaks are observed in Gonio scan. As a remark, the peak at (10\overline{1}1) which is 2.5 times stronger than that at (1\overline{1}00), according to the standard ErSi₂ powder diffraction data [9], is absent. This result indicates that the ErSi₂ film has a preferred orientation to the substrate [10]. The ErSi₂ (1\overline{1}00) and (2\overline{2}00) peaks are absent in the GI scan. Since the GI scan cannot detect the crystal planes that are parallel with the substrate surface, the contrasting findings in the two scans suggest that the ErSi₂ (1\overline{1}00) lattice planes are placed in parallel to Si (001) direction [11]. The ErSi₂ (1\overline{1}00) and (2\overline{2}00) peaks disappear in the samples that were RTA annealed at 550 °C or above, while the peaks of Er₂O₃ at (211), (222), (400) and (440) are present for all samples after the RTA annealing. In addition, it is also observed that those XRD peaks corresponding to Er₂O₃ become more and more noticeable with increasing RTA temperatures.

Therefore, from the Gonio and GI scan results of Sample E1, we find that ErSi₂, having a preferred orientation with the substrate (001)Si, (i.e., (1\overline{1}00)ErSi₂/(001)Si), only appears at 500 °C and that Er₂O₃ is the favored phase to form in this set of the samples after RTA.
**Fig. 4.2** XRD spectra for Sample E1 annealed at different temperatures ranging from 400 °C to 800 °C in N₂ ambient for 1 minute (a) Gonio scan and (b) GI scan.
Figures 4.3 (a) and 4.3 (b) depict the Gonio and GI scan results of Sample $E2$, which were prepared with a lower base pressure during the sputtering process, before and after the RTA treatment. Similar to the results in Fig. 4.2 for Sample $E1$, the peaks corresponding to $Er_2O_3$ (222), (400) and (440) are present in all RTA-annealed samples. There are, however, two major differences between the results of Sample $E1$ and $E2$. The first difference is that the Er (002) peak in as-deposited Er film is much stronger in Sample $E2$ than in $E1$. This plot, together with the XRD GADDS scans images for the as-deposited samples in Figs. 4.4 (a) and 4.4 (b), implies that the Er film deposited with lower base pressure has a higher degree of texture as compared to the Er film deposited with higher base pressure. This is most likely due to less oxygen incorporation in the as-deposited Er film with a low base pressure. The second difference is related to the temperature window for $ErSi_2$ formation. As shown by the Gonio scan results, $ErSi_2$ (1 100) and (2 2 00) peaks only appear after RTA at 500 °C in Sample $E1$; however, those peaks are present in Sample $E2$ after RTA at temperatures ranging from 400 °C to 650 °C. The comparison between Figs. 4.2 and 4.3 shows that the $ErSi_2$ phase is more easy to form with less oxygen incorporation during Er sputtering deposition (due to lower base pressure), which in turn clearly demonstrates the significant effect of oxygen incorporation during Er deposition on $ErSi_2$ formation in subsequent RTA silicidation process.

FWHM (Full width at half maximum) of XRD peak corresponding to $ErSi_2$ (1 100) in Sample $E2$ (0.51°) is found smaller than that for Sample $E1$ (0.74°) (both samples were annealed at 500 °C). The sharper XRD peak for Sample $E2$ that was prepared under low base pressure indicates that the $ErSi_2$ films formed in this sample have an improved texture. Therefore, we may conclude that, other than on the $ErSi_2$ formation, oxygen incorporation during Er deposition also has a significant influence...
on the quality of the erbium disilicide films.

Fig. 4.3 XRD spectra for E2 annealed at different temperatures ranging from 400 °C to 800 °C in N₂ ambient for 1 minute (a) Gonio scan and (b) GI scan.
4.3 TEM Results

Transmission electron microscopy examinations were performed on the cross-sections of ErSi$_2$ samples grown on (001)Si using Phillips 400 TEM. Figure 4.5 (a) shows a cross-section TEM (XTEM) image of Sample E1, which was annealed at 500 °C in N$_2$ for one minute. The result indicates that there are three distinct layers above the Si substrate. The layer adjacent to the Si substrate is dark in the TEM image and is characterized by parallel lines. The distance between the parallel lines is found to agree with that of (1100) plane of ErSi$_2$, suggesting that the layer is ErSi$_2$ and that it is epitaxial with (001)Si. The TEM result is consistent with our earlier finding from the XRD analyses. In contrast to the first layer that is characterized by parallel lines, the second layer lacks a clear pattern of ordered atomic arrangement, which implies that the second layer is an amorphous structure. The amorphous interlayer should be an Er and Si intermixing layer according to previous study [12-14] and it will be confirmed later in Sec.4.4 by SIMS characterization. The third layer is similar to the
first one that shows the characteristics of a highly textured or epitaxial structure. According to our XRD analyses, only ErSi₂ and Er₂O₃ formed in this sample with highly textured orientation and, thus, we conjecture that this layer should be Er₂O₃. This will also be demonstrated later by SIMS analysis.

Figure 4.5 (b) presents the HRTEM image of Sample E₂ undergoing the same annealing process as Sample E₁. It is found that the structures of the two samples are similar: both contain three layers above Si substrate, namely a textured or epitaxial ErSi₂ layer, an amorphous layer, and a textured Er₂O₃ layer.

The observation of the three layered structure is indeed expected for the Er/(001)Si system after solid phase reaction. It is well known that during the solid phase reaction of Er with Si(001), an amorphous Er/Si (a-Er/Si) interlayer is the first phase to form [12, 13]. This is followed by the nucleation of ErSi₂ at the interface between the amorphous interlayer, a-Er/Si, and the (001)Si substrate. At the same time, the amorphous interlayer keeps growing by consuming the pure Er layer. In addition, the unreacted Er layer also reacts with the oxygen coming from the N₂ ambient to develop a textured Er₂O₃ layer on top of the Er layer. Accordingly, there are four layers present above the Si substrate during the annealing process, which follows the sequence of ErSi₂, amorphous interlayer, Er, and Er₂O₃ as moving away from the substrate. The unreacted Er layer would be eventually consumed by the amorphous interlayer a-Er/Si and the Er₂O₃ layer after certain annealing time, leading to a triple layer structure of ErSi₂ – a-Er/Si – Er₂O₃ as revealed by the XTEM images.
Fig 4.5 HRTEM images of Sample (a) E1 and (b) E2 annealed at 500 °C in N₂ for one minute.
It is found that the thickness of the a-Er/Si layer in Sample E2 is considerably thinner than that in Sample E1, while the thicknesses of the Er$_2$O$_3$ layers are almost identical in the both samples. Since the total amount of Er deposited on the substrate is the same in the two samples, a thinner amorphous layer in Sample E2 implies that the ErSi$_2$ layer in the E2 sample is thicker. The result is consistent with the XRD observation that the XRD peaks corresponding to ErSi$_2$ phase in the E2 sample is much stronger than that in the E1 sample. On the other hand, the observation of
identical thickness of $\text{Er}_2\text{O}_3$ layer in the two samples indicates that the $\text{Er}_2\text{O}_3$ formation process is mainly controlled by the oxygen partial pressure in the annealing $\text{N}_2$ ambient rather than the amount of oxygen incorporated into Er during sputtering.

Figure 4.6 shows selected area electron diffraction (SAED) pattern taken on the ErSi$_2$ layer in the E2 sample annealed at 500 °C. The blue circles in the figure represent the electron diffraction spots from Si substrate, and the purple and the yellow ones correspond to those from hexagonal ErSi$_2$ epitaxially grown on (001)Si. In the epitaxial growth of ErSi$_2$ on (001)Si, ErSi$_2$ takes the hexagonal structure of AlB$_2$ with its c-axis aligning with the [01$\bar{1}$] or the [011] directions in the (001)Si plane. The diffraction patterns of the ErSi$_2$ structures resulting from the two possible orientations are different, and they are indicated by the two colours in the figure (the details of the epitaxial growth of ErSi$_2$ on (001) Si is discussed earlier in Chapter 2.). The SAED patterns are compared with the simulation result in Ref. [10], which presented the diffraction patterns of the hexagonal ErSi$_2$ structure along the [0001] and [2$\bar{1}$10] zone axes and the pattern of Si along the [011] zone axis. The two sets of diffraction patterns of ErSi$_2$ measured from our samples are found to match well with the simulation result, in terms of the distance scale between the Si spots and ErSi$_2$ spots and their relative locations to each other. The good agreement verifies that the ErSi$_2$ in our samples is of the AlB$_2$ structure. The agreement also confirms that ErSi$_2$ grew epitaxially on the Si substrate in our experiment. And ErSi$_2$ layer is epitaxial to the Si(001) with two different epitaxial orientation relationships:

(a) ($0\bar{1}10$) ErSi$_2$ // (001) Si, [0001] ErSi$_2$ // [011] Si, [2$\bar{1}$10] ErSi$_2$ // [01$\bar{1}$] Si

(b) ($0\bar{1}10$) ErSi$_2$ // (001) Si, [0001] ErSi$_2$ // [011] Si, [2$\bar{1}$10] ErSi$_2$ // [011] Si,

which is in agreement with the previous reports [3, 10].
4.4 SIMS results

Figures 4.7 (a) and 4.7 (b), respectively, plot the SIMS results of Sample E1 and E2 right after the deposition process. It can be seen from the figures that no noticeable inter-diffusion between Er and Si occurred at Er/Si interface, suggesting that Er deposition does not induce the formation of Er-Si compound or any silicide phase at room temperature. While the high oxygen signal intensities near the very top surface in the both samples are probably due to artifact related to surface effect, the comparison between the results of the two samples clearly shows that there is significantly more oxygen present in as-deposited Er film of Sample E1, as compared to Sample E2, obviously owing to the high base pressure for the sputtering deposition of Er in Sample E1 (4x10⁻⁶ torr, as compared to 5x10⁻⁷ torr for E2).

Figures 4.8 (a1) - (a3) depict the elemental depth profiles of Sample E1, after annealing at 400 °C, 500 °C and 600 °C, respectively; while Figs. 4.8 (b1) - 4.8 (b3) plot the results of Sample E2 after annealing at the same temperatures. All of the figures suggest that there is an inter-diffusion between the erbium and silicon...
happened in all the samples after RTA process. According to the previous study [15] in the Er/Si system, Si is expected to be the dominant diffusing species during intermixing because the Si bonds near the surface are weakened by the adsorption of Er atoms. As a result, the silicon atoms are released to form the amorphous interlayer. It has been addressed by several authors that the amorphous interlayer has an important influence on the silicide nucleation, the sequential growth of silicide phases, the surface roughness and the Schottky barrier height [13, 16-18].

Comparing Figs. 4.8 (a1) and 4.8 (b1) with Figs. 4.7 (a) and 4.7 (b), it can be seen that the signal of oxygen in the samples annealed at 400 °C increased dramatically in the upper region of the original Er layer. This observation indicates that significant oxidation of Er by residual oxygen in the N2 ambient had took place in the Er layer during RTA process. The strong oxidation of Er by residual oxygen even at 400 °C, which results in the formation of Er2O3 (seen XRD results in Fig. 4.2 and Fig. 4.3), is certainly due to high chemical activity of Er [19-21]. Although strong oxidation of Er by residual oxygen is observed for both Sample E1 and E2 annealed at 400 °C, the two samples also exhibit significant differences with respect to the intermixed layer formation. First, the intermixing layer of Er and Si is thinner for Sample E1 than that for E2. This finding may be related to the presence of thicker interfacial oxide layer for Sample E1. From the previous report [13], interfacial oxides are believed to affect the formation of the intermixing Er/Si layer by minimizing its intermixing speed. Second, there is a thin ErSi2 layer formed on the E2 sample. The formation of ErSi2 in Sample E2 can be confirmed by the ratio between the Si and the Er signal intensities from the depth profiles. Additionally, the XRD results depicted earlier in Fig. 4.3 (a) also suggest the existence of the ErSi2 phase, and the TEM images illustrate that an epitaxy ErSi2 layer forms next to Si substrate.
In summary, for the $E_1$ sample annealed at 400 °C, most of Er turned into $\text{Er}_2\text{O}_3$ by reacting with the oxygen diffusing into Er/Si from the RTA ambient and an amorphous interlayer of Er/Si/O is present between the top layer and substrate. In comparison, for Sample $E_2$, there are three regions observed on the top of the Si substrate: an erbium oxide layer, an inter-diffusion amorphous layer consisting of Er, Si, and O, and a very thin ErSi$_2$ layer.

The SIMS depth profiles of Sample $E_1$ and $E_2$ annealed at 500 °C are shown in Figs. 4.8 (a2) and 4.8 (b2), respectively. The intermixing layers of Er and Si for Sample $E_1$ and $E_2$ annealed at 500 °C become broader compared with the samples annealed at 400 °C. This suggests that Si interfuses into Er/Si system deeper/faster with the annealing temperature increasing. Similarly with the results of $E_2$ at 400 °C annealing, Figs. 4.8 (a2) and 4.8 (b2) indicate three different layers developed during the RTA process at 500 °C in both samples, which are the erbium oxide layer, the amorphous inter-diffusion layer, and ErSi$_2$ layer. Figures 4.8 (a2) and 4.8 (b2) also suggest that the ErSi$_2$ layer in Sample $E_2$ is thicker than that in Sample $E_1$. This is in agreement with our earlier XRD result (stronger ErSi$_2$ (1100) peaks observed on $E_2$) and TEM result (thicker ErSi$_2$ layer seen from $E_2$).

Figures of 4.8 (a3) and 4.8 (b3) illustrate the depth profiles of Sample $E_1$ and $E_2$ annealed at 600 °C. The depth profile of the $E_2$ sample is similar to those $E_2$ with 400 and 500 °C annealing, while the $E_1$ sample with 600 °C annealing lacks the ErSi$_2$ layer according to the ratio between Er and Si signal intensities in the figure. These observations are again consistent with the according XRD results in Fig 4.2 that no ErSi$_2$ peaks are observed on the 600 °C annealed $E_1$ sample while they present in the $E_2$ sample after the same temperature annealing. In addition, the intermixing Er/Si layer become thinner with further high annealing temperature compared with the
results of the samples annealed at 500 °C. The intermixing layer is important to the formation of ErSi$_2$ layer [13, 22]. Therefore, thinner intermixing Er/Si layer may attribute to the absent of ErSi$_2$ layer of Sample E1.

It is important to note that the oxygen content is high in the amorphous Er/Si interlayer for all annealed samples (except for the 400 °C annealed E1 and E2 samples), suggesting that the oxygen solubility in the Er/Si interlayer is high. In contrast, it appears that the oxygen concentration in the epitaxial ErSi$_2$ layer is extremely low. The fact that almost the same oxygen signal intensities were observed for the 500 and 600 °C annealed E1 and E2 samples further implies that the oxygen content in the Er/Si layers might have reached its solubility limit after 60 s RTA at 500 and 600 °C.
Fig. 4.8 Depth profiles for Sample E1 annealed at (a1) 400 °C, (a2) 500 °C, and (a3) 600 °C and Sample E2 annealed at (b1) 400 °C, (b2) 500 °C, and (b3) 600 °C.
4.5 Discussion: the effects of oxygen incorporations on ErSi₂ formation

The experimental results presented in the previous sections clearly show the important role of oxygen incorporated either during Er sputtering deposition or from annealing ambient during RTA in ErSi₂ formation. Summarizing important experimental observations: (1) the Er film sputter-deposited with higher base pressure contains more residual oxygen and is less textured; (2) the formation of ErSi₂ is suppressed when oxygen concentration in the as-deposited Er is high, i.e., a delayed formation of ErSi₂ at low temperature end (500 °C vs. 400 °C) and an earlier absence of ErSi₂ at high temperature end (500 °C vs. 650 °C), resulting in a narrow formation temperature window; (3) the amorphous Er/Si interlayer has a high oxygen solubility while it appears extremely low in ErSi₂ layer; and (4) a significant oxidation of Er by residual oxygen in the annealing ambient occurs during RTA annealing with N₂ as ambient gas. It seems that the increase in the lowest temperature for ErSi₂ formation is a sensitive function of the concentration of oxygen incorporated during Er-sputtering deposition, probably due to the dependence of ErSi₂ nucleation/growth processes on the O concentration in the amorphous Er/Si interlayer. On the other hand, it is most likely that oxidation by the residual oxygen in the N₂ ambient during RTA is directly held responsible for inhibiting the formation of ErSi₂ at high annealing temperature. It is not obvious at first glance why the upper limit of the formation temperature is also dependent on the amount of initial oxygen incorporated into Er during the sputtering deposition. However, noting that the as-deposited Er that is deposited with lower base pressure shows higher degree of texture, it is believed that the dependence of the upper-limiting ErSi₂ formation temperature on the original amount of oxygen in the as-deposited Er is related to the dependence of oxygen diffusivity on the
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microstructure of as-deposited Er, i.e., the degree of texture in the Er layer.

In order to explain these points, it is essential to analyze the kinetic processes involved in the formation of ErSi$_2$ first. As discussed previously, there are three kinetic processes involved in the formation of ErSi$_2$: (1) the formation/growth of an amorphous Er/Si interlayer between Er and Si by the diffusion of Si upon annealing, (2) the nucleation/growth of ErSi$_2$ at the interface between the Er/Si interlayer and Si, and (3) the oxidation of Er surface by residual oxygen in N$_2$ annealing ambient. In addition, it is believed that there is a diffusion of oxygen from Er-oxide into the amorphous Er/Si layer (through the unreacted Er if Er is not consumed by the growing Er$_2$O$_3$ and the amorphous Er/Si interlayer).

From the fact that significant amount of ErSi$_2$ is formed on Sample E2 after RTA annealing at 400 °C, it can be deduced that the oxidation of Er by residual oxygen in N$_2$ is rather fast process even at low temperature. On the other hand, it appears that the formation of the amorphous Er/Si interlayer is delayed by the oxygen present in Er (at least at low processing temperatures, e.g., 400 °C) while the nucleation/growth of ErSi$_2$ is even more greatly suppressed by the presence of oxygen in the amorphous Er/Si layer (probably due to the fact that the oxygen is repelled from the growing ErSi$_2$ into a-Er/Si(O) layer, thus further increasing the oxygen content in the a-Er/Si(O) layer). With a higher oxygen content in Er on Si, the formation of the amorphous Er/Si(O) interlayer, which competes with the Er oxidation by the residual oxygen in N$_2$ to consume, would be delayed at low annealing temperatures (e.g., 400 °C). Due to this delay in the formation of the amorphous Er/Si(O) interlayer, only a very thin Er/Si(O) interlayer forms as observed in the 400 °C annealed E1 sample. In this case, the nucleation of ErSi$_2$ would also be suppressed, due to the increased nucleation barrier in the presence of substantial amount of oxygen in the amorphous
Er/Si(O) interlayer, thus explaining the absence of ErSi₂ in the 400 °C annealed E₁ sample (note: with pure Er on Si, the onset temperature for ErSi₂ formation is typically 300 °C [11]).

Now turning to the failure to form ErSi₂ with RTA at high temperatures (i.e., temperatures higher than 500 °C for the E₁ samples and 650 °C for the E₂ samples), we explain the experimental observation on the viewpoint of the faster increase in oxygen diffusion through unreacted Er layer with increasing annealing temperature as compared to the increase in the ErSi₂ nucleation rate. As we discussed before, during the annealing, the formation/growth of the amorphous Er/Si(O) interlayer and the surface oxidation of Er by the residual oxygen in N₂ occurs simultaneously. At the same time, oxygen diffusion from the oxidized top Er layer into the amorphous Er/Si(O) interlayer through the unreacted Er layer (sandwiched between the oxidized top Er layer and the growing Er/Si(O) interlayer) would take place. If the activation energy for such a diffusion is significantly higher than those for ErSi₂ nucleation, for a sufficiently high annealing temperature, one would expect a fast saturation of the oxygen in the Er/Si(O) interlayer even before any ErSi₂ nucleation. The saturation of the Er/Si(O) interlayer would in turn completely prohibit the ErSi₂ nucleation due to much increased nucleation barrier, thus explaining the absence of ErSi₂ in the higher temperature annealed samples (≥ 600 °C for the E₁ samples and ≥ 700 °C for the E₂ samples). It is also speculated that the oxygen diffusion through the unreacted Er is much lower with highly textured Er due to the presence of less fast diffusion paths such as grain boundaries. Therefore, the critical temperature at which the saturation of the Er/Si(O) interlayer with oxygen takes place before ErSi₂ nucleation would be higher than that with less textured Er layer as observed in the E₂ samples (700 °C vs. 600 °C with the E₁ samples).
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4.6 Conclusion

To study the influence of oxygen incorporation in the erbium silicidation process, experimental results of the samples prepared under low and high vacuum conditions, annealed at different temperatures ranging from 400 °C to 800 °C, are presented and discussed in this chapter.

The experimental results presented clearly showed that the oxygen incorporated into Er during sputtering-deposition has a significant effect on the formation of ErSi$_2$ as the formation of ErSi$_2$ was observed only after 500 °C RTA in the E1 samples (prepared with higher base pressure) while the presence of ErSi$_2$ was evident in the E2 samples (prepared with lower base pressure) after RTA at temperatures ranging from 400 °C to 650 °C. XRD and TEM results showed that the formed ErSi$_2$ films are epitaxial on the (001)Si substrates with orientation relationships: (a) (0 1 1 0) ErSi$_2$∥(001) Si, [0001] ErSi$_2$∥[011] Si, [2 1 1 0] ErSi$_2$∥[01 1] Si; (b) (0 1 1 0) ErSi$_2$∥(001) Si, [0001] ErSi$_2$∥[01 1] Si, [2 1 1 0] ErSi$_2$∥[01 1] Si. TEM and SIMS results also revealed that there exist three distinct regions of erbium oxide, amorphous interlayer of erbium and silicon with oxygen and epitaxial ErSi$_2$ on silicon substrate.

As the formation of top Er oxide layer is due to oxidation of Er by the residual oxygen in the N$_2$ annealing ambient, the experimental results clearly show that the formation of ErSi$_2$ is influenced both by the presence of oxygen in as-deposited Er (incorporated during sputtering deposition) and by the attack by the residual oxygen in the N$_2$ ambient during the annealing. From the comprehensive analysis, the influence of the oxygen that is incorporated into as-deposited Er during the sputter-deposition on the processing temperature window for ErSi$_2$ is explained in terms of the increase in ErSi$_2$ nucleation barrier with the presence of oxygen in the amorphous Er/Si(O) interlayer.
and the fast saturation of the Er/Si(O) with oxygen that is diffused from the top Er oxide layer, through the unreacted Er layer, into the Er/Si(O) interlayer even before ErSi$_2$ nucleation at high processing temperatures as well as the influence of the incorporated oxygen on the microstructure of as-deposited Er and resulting effect on the oxygen diffusion through the unreacted Er layer.

To further study the oxygen influence during the silicidation process, the using of a Ti capping layer will be discussed in the next chapter.
References


Chapter 5

The Effects of the Capping Layer on Erbium Silicide Formation

From the previous work, we found that the ErSi$_2$ formation is sensitive to the presence of oxygen. Oxygen incorporation (or contamination) may originate from different sources such as the RTA process and the Er sputtering process. Obviously, in order to obtain high quality ErSi$_2$ films, it is imperative to suppress the detrimental effect of oxygen incorporation.

A possible solution to the oxygen contamination is proposed to deposit a Ti film as a capping layer after the sputtering deposition of Er film. This approach has been used for the growth of cobalt silicide, which has similar oxygen contamination problem. It is found that the Ti capping layer can reduce oxygen contamination coming from the interfacial oxide or from the RTA ambient [1, 2]. The Ti capping layer has also been demonstrated to be able to improve the film quality of cobalt silicide [1, 3]. Motivated by the promising findings, we investigated the effect of Ti capping layer on the growth of Er silicide.

The structure of the samples considered in this chapter is depicted in Fig. 5.1, which consists of a Si substrate, a 35-nm Er film, and a 15-nm Ti capping layer. Two types of the samples with the same structure were prepared under different base pressures during the sputtering of Er film. For the first set of the samples, labeled as TE1, the base pressure was $4 \times 10^{-6}$ torr before sputter deposition; for the second set of the samples, labeled as TE2, the base pressure was $5 \times 10^{-7}$ torr. After metallization,
the samples were annealed for 60s at temperatures ranging from 400 to 800 °C. The samples were then analyzed by means of XRD, XPS, SIMS, TEM, and SEM.

5.1 XRD results

The phases of Er silicide films formed on the samples with Ti capping layers were examined by using XRD. Gonio scans, GI X-ray diffraction spectrometry and rocking curve measurements were carried out using Bruker AXS GmbH 2000 system equipped with a Cu-kα radiation operating at 40 kV and 45 mA.

Figures 5.2 (a) and 5.2 (b), respectively, plot the XRD Gonio and GI scans for Sample TE1 after RTA at different temperatures. The results show that peaks corresponding to (400)Er₂O₃ are detectable in the all RTA-annealed samples. It is also found that peaks corresponding to (1 1 0 0) and (2 2 0 0) ErSi₂ are present in the samples annealed at temperature ranging from 500 to 700 °C, confirming the formation of epitaxial ErSi₂ in this temperature range. Compared to Sample E1, in which ErSi₂
formation was observed only in the sample annealed at 500 °C. Sample \textbf{TE1} shows a much larger processing window for ErSi$_2$ formation, 500 – 700 °C, which is obviously due to the presence of the Ti capping layer. It is also worthy to note that the intensity of the ErSi$_2$ peaks in the 500 °C annealed \textbf{TE1} sample is 2.5 times stronger than that in the 500 °C annealed \textbf{E1} sample. This result indicates that a much thicker ErSi$_2$ formed when a Ti capping layer is present on top of Er to protect Er from oxygen attack during RTA process.

Figures 5.3 (a) and 5.3 (b) depict the Gonio and GI scan results of the \textbf{TE2} samples, which were prepared under a lower base pressure during the sputtering process. Both scans show that the peaks corresponding to TiO are present. The scans also indicate that Er$_2$O$_3$ (222) peaks become stronger as the RTA temperature increases. The two findings suggest that it is more favorable for oxygen to react with Ti than with Er although it is also true that oxygen can diffuse underlying Er layer to form Er$_2$O$_3$. Besides the TiO and Er$_2$O$_3$ peaks, strong peaks corresponding to ErSi$_2$ (1100) and (2200) are also present with the RTA temperatures between 400 and 800 °C, again showing that the processing window for ErSi$_2$ is significantly widened by the presence of the Ti capping layer (400-800 °C for the \textbf{TE2} samples vs. 400-650 °C for the \textbf{E2} samples).

The film crystallinity of the ErSi$_2$ films was investigated using the FWHM of the rocking curve around ErSi$_2$ (1100) (at $2\theta \approx 27.081$) diffraction peak, which is the distance between points on the curve at which the function reaches half maximum value [4]. Using this characterization method, the quality and texture of ErSi$_2$ thin film formed can be predicted and analyzed. A sharper shape of the rocking curve which means a smaller FWHM implies a higher crystallinity.
Fig. 5.2 XRD spectra for Sample TE1 annealed at different temperatures ranging from 400 °C to 800 °C in N₂ ambient for 1 minute (a) Gonio scan and (b) GI scan.
Fig. 5.3 XRD spectra for Sample TE2 annealed at different temperatures ranging from 400 °C to 800 °C in N₂ ambient for 1 minute (a) Gonio scan and (b) GI scan.
Figures 5.4 (a) and 5.4 (b), respectively, show the rocking curves of Samples \textbf{TE2} and \textbf{E2} annealed at different temperatures with the maximum in the curves corresponding to ErSi$_2$ (1$ar{1}$00) (20 $\approx$ 27.081). According to the measurements of the FWHM for ErSi$_2$ (1$ar{1}$00), Fig. 5.4 (c) plots the variation of FWHM of the rocking curves as a function of annealing temperature. As shown in Fig.5.4 (c), the FWHM value in Sample \textbf{E2} is reduced (which means that the crystallinity of the ErSi$_2$ film is improved) when the annealing temperature is increased from 500 to 600 °C. When the temperature is further raised to 650 °C, however, the FWHM becomes larger (which implies the degradation in the film crystallinity). The variation of FWHM with the temperature in \textbf{TE2} is similar to that in \textbf{E2}: FWHM decreases with increasing temperatures until the temperature reaches a high value. The FWHM value first decreases quickly when the temperature is raised from 500 to 600 °C and then the reduction in the FWHM value becomes much smaller when the temperature is increased from 600 to 750 °C. Finally, the FWHM value starts to increase when the temperature changes from 750 to 800 °C. It is important to note that the FWHM values of the \textbf{TE2} samples are significantly lower than those of the \textbf{E2} samples for most of the annealing temperatures considered in our study. This demonstrates that the Ti capping layer can improve the crystallinity (or texture) of the ErSi$_2$ film drastically.

In addition to the film texture, it appears that the Ti capping also affects the ErSi$_2$ formation temperature. By comparing the XRD results, it is found that ErSi$_2$ formation temperature is lower in the \textbf{TE2} samples than that of the \textbf{E2} samples, as shown in Figs. 5.3 (a) and 4.3 (a). In particular, Fig. 4.3 (a) indicates Sample \textbf{E2} annealed at 400 °C has weak peak corresponding to (1$ar{1}$00) of the ErSi$_2$ phase. In contrast, a much stronger ErSi$_2$ (1$ar{1}$00) peak is present in the XRD pattern obtained on the 400 °C annealed \textbf{TE2} sample. The observation of a significantly stronger ErSi$_2$
(1\overline{1}00) peaks implies that the lowest formation temperature of ErSi$_2$ is reduced in the TE2 samples due to the presence of the Ti capping layer.

![Fig. 5.4](image)

**Fig. 5.4** Rocking curve plots of ErSi$_2$ (1\overline{1}00) (at 2\theta \approx 27.081) for samples (a) TE2 and (b) E2 samples annealed at different temperatures and (c) relationship of FWHM of rocking curves as a function of annealing temperature for TE2 and E2.
5.2 Role of the Ti in erbium silicidation process

The XRD results presented in the previous section clearly showed the beneficial effects of the Ti capping layer, which include (1) reducing the minimum formation temperature of erbium disilicide, (2) enlarging processing window for ErSi$_2$ formation i.e., the temperature range for ErSi$_2$ formation, and (3) improving the ErSi$_2$ film crystallinity (or texture). The role of the Ti in erbium silicidation process is examined in this section in order to understand these beneficial effects of the Ti capping.

X-ray photoelectron spectrometry (XPS) characterization using the Al K$_\alpha$ radiation was performed on E1, E2, TE1 and TE2 to determine the film composition. Figure 5.5 presents the Ti 2P spectra on the Ti surface of the as-deposited TE1 sample. The result shows the presence of a TiO$_x$ layer, even though no peaks corresponding to TiO$_x$ were observed in the XRD measurement. It is believed that this titanium oxide probably acted as either (or both) an oxygen diffusion barrier (or and) oxygen getter, protecting the underlying unreacted erbium from oxygen contamination.

Fig. 5.5 The Ti 2P spectra for as-deposited sample of TE1.
Figures 5.6 (a) and 5.6 (b) plot the O 1s spectra at the Ti/Er interface of the TE1 and TE2 samples while Figs. 5.6 (c) and 5.6 (d) illustrate the same spectra at the depth of 5-10 nm of the Er layer of Sample E1 and E2. Comparison between Figs. 5.6 (a) and 5.6 (c) indicates that the intensity of the O 1s signal is much lower in the TE1 sample, suggesting that the incorporation of oxygen in the bulk of Er film is reduced by introducing the Ti capping layer. The peak corresponding O 1s disappears in the as-deposited TE2 sample, which means a capping layer together with low base pressure for sputter-deposition is an effective way to minimize (or even almost completely remove) the incorporated oxygen in the as-deposited Er film.

**Fig. 5.6** The O 1S spectra for the as-deposited sample and sample annealed at 400 °C of (a)TE1, (b) TE2, (c) E1, and (d) E2.
5.3 SIMS results

Figures 5.7 (a) and 5.7 (b), respectively, plot the SIMS results of the TE1 and TE2 samples right after the Er sputter-deposition. Comparison between the results from the two samples shows that oxygen signal in the Ti layer is much stronger in TE1 than in TE2, which is due to the fact that TE1 was prepared with a much higher base pressure and thus more oxygen was incorporated into Ti during the sputtering deposition. Contrary to the Ti layer, the oxygen content incorporated in Er layer in the TE1 sample is comparable with that in the TE2 sample. However, the oxygen signal intensity is increased substantially at the Er/Si interface of the TE1 sample, which is similar to the finding in Sample E1 (without capping layer) as shown in Fig. 4.7 (a). This finding suggests that the Ti capping layer may not be able to eliminate the interfacial oxide layer as effectively as low sputtering base pressure does, at least at room temperature. From the figures, it also can be seen that the Si distribution profiles in the two samples are similar: the Si signal increases sharply from virtually zero level to a high and constant level near the Er/Si interface, suggesting that no inter-diffusion between Er and Si occurred after the deposition of Er (on to Si) and Ti (on top of

(a) E1: as-deposited  
(b) E2: as-deposited  

Fig. 5.7 Depth profiles for Sample (a) TE1 and (b) TE2 for the as-deposit samples.
Figures 5.8 (a1)-5.8 (a3) depict the elemental depth profiles of the \textbf{TE1} samples, after annealing at 400 °C, 500 °C and 600 °C, respectively while Figs. 5.8 (b1)-5.8 (b3) plot the results of the \textbf{E2} samples after annealing at the same temperatures. Similar to the samples without Ti capping, inter-diffusion between the erbium and silicon is observed in these six annealed samples. However, comparing the Si depth profiles in Fig. 5.8 (the samples with a capping layer) with those shown in Fig. 4.8 reveals that Si diffuses deeper (faster) into Er to form the intermixing phase of Er/Si as well as ErSi₂. In addition, the intermixing region of Si and Er is thicker in the samples with the Ti capping layer than those without the layer. This suggests that Ti capping impedes oxygen from diffusing into the Er layer. As the oxidation of Er is suppressed, it becomes easier for Si to diffuse into the Er layer, resulting in larger intermixing region of Er/Si. Since the intermixing layer (or region) is the precursor for the formation of ErSi₂ as we discussed in Chapter 4 [5, 6], the ErSi₂ phase can form at lower temperatures if it is easier for Si to diffuse into the Er layer to develop the intermixing layer.
Chapter 5 The Effects of the Capping Layer on Erbium Silicide Formation

![Depth profiles for Sample TE1 annealed at (a1) 400 °C, (a2) 500 °C, (a3) 600 °C and Sample TE2 annealed at (b1) 400 °C, (b2) 500 °C, (b3) 600 °C.](image)

**Fig. 5.8** Depth profiles for Sample TE1 annealed at (a1) 400 °C, (a2) 500 °C, (a3) 600 °C and Sample TE2 annealed at (b1) 400 °C, (b2) 500 °C, (b3) 600 °C.
5.4 Film morphology study

Figure 5.9 shows the surface morphology images of Sample E1 annealed at 500 °C of different magnitude. Square defects are found nonuniformly distributed on the film surface. The size of the defect is about 3-4 µm. As discussed in Chapter 2, ‘pits’ or ‘pinholes’ are common in rare-earth silicide films formed by solid phase reactions of rare earth metals and Si [7-9]. The pits are of considerable lateral extent and penetrate deeply into the Si substrate relative to the silicide thickness. The shape of these defects is inherited from the substrate structure: triangular on Si(111) and square on Si(001) [8]. It is important to point out that the defects observed in this study on ErSi₂ films formed by rapid thermal annealing of Er films on Si(001) substrates also show square shape (from top-view). However, it appears that the defects observed in Er-silicide films formed by RTA are different in nature from those pits or pinholes reported previously on ErSi₂ films formed by furnace annealing with prolonged annealing times. The cross-sectional TEM revealed that the defects observed in our study have a pyramidal shape with the apex directed away from the substrate, as shown in Fig. 5.10.

Fig. 5.9 SEM images of Sample E1 after RTA for one minute annealed at 500 °C.
Fig. 5.10 Typical cross-sectional TEM image of the structural defects observed in ErSi$_2$ films formed by rapid thermal annealing of Er films on (001)Si substrates.

Figures 5.11 (a)-(e) present the surface morphology of Sample TE1 after RTA process at temperatures ranging from 500 °C to 700 °C, using SEM observation. Similarly, these defects all have nearly square bases and all of the defects share the same orientation. These images also show that surface defects coverage increases with the annealing temperature increasing at first and becomes decreasing at temperatures higher than 600 °C. These defects are believed to be associated with the erbium silicidation process, due to the fact that only samples with ErSi$_2$ (verified by XRD) display such pyramidal defects. In addition, the presence of these defects in all samples, independently of whether the film was capped with Ti or not, indicates that the formation of these defects is not associated with oxidation. Comparing with the surface images of the samples without Ti capping layer (E2), the observed defects on the surface (with the same annealing condition, eg. 500 °C) are less on the samples with Ti capping. This comparison indicates that Ti capping may help to improve the surface defects of Er/Si system after solid phase reaction.
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(a) 500 °C

(b) 550 °C

(c) 600 °C
Fig. 5.11 SEM images of Sample TE1 after RTA for one minute annealed at (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C and (e) 700 °C.

Possible mechanism of such defects has been proposed by Tan et al [10]. Tan et al studied the thin film of epitaxial ErSi₂ formed by annealing Er films on (001)Si substrates at temperatures ranging from 500 °C to 800 °C. From the investigation of the XTEM of pyramidal defects, they propose that these defects form as a result of the separation of the silicide film from the substrate and its buckling in
order to relieve the compressive, biaxial epitaxial stresses. Silicon can then diffuse through the silicide or along the interface to fully or partially fill the void between the buckled ErSi$_2$ film and the substrate, as shown in Fig. 5.12.

![Fig. 5.12](image)

**Fig. 5.12** Schematic representation of the formation and evolution of the pyramidal defect, showing (a) the initial compressively stressed ErSi$_2$ film on a Si substrate, (b) the buckling of the silicide film and its separation from the substrate, (c) Si diffusion along Si(001) surface and within the ErSi$_2$ film, and (d) the formation of a crack in the pyramidal defect.
5.4 Conclusion

Ti capping layer has been demonstrated to have a beneficial influence on the formation of erbium silicide films as it decreases the temperature of ErSi$_2$ formation; it broadens the process window of ErSi$_2$ formation; and also it improves the film texture. This beneficial effect of Ti capping is attributed to the suppressed incorporation of the oxygen in the bulk of Er film from the annealing ambient (Ti readily reacts with oxygen) during the RTA silicidation as well as the oxygen-gettering ability (to getter already incorporated oxygen in Er) of Ti due to its chemical activity. In addition, the possible mechanism of pyramidal defects on film surface was discussed. The using of Ti capping layer appears to help to reduce such defects although the exact reason is not clear at the moment. Future work will be needed to explore the cause for Ti to reduce the defects.
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Chapter 6

Conclusion and Future Work

6.1 Conclusion

In our study, the influence of oxygen incorporation (from different sources such as the RTP process and the sputtering process) on the formation mechanism of erbium disilicide and a possible solution to the oxygen contamination problem (using Ti capping layer) have been investigated.

The study on the samples prepared with different base pressures in the Er sputtering deposition process shows that oxygen incorporated into Er has a significant effect on the formation of ErSi$_2$. Epitaxial ErSi$_2$ film has been demonstrated to grow on the (001)Si substrate in our work. The formation of ErSi$_2$ is influenced both by the presence of oxygen in as-deposited Er (incorporated during sputtering deposition) and by the attack by the residual oxygen in the N$_2$ ambient during the annealing. From the comprehensive analysis, the influence of the oxygen that is incorporated into as-deposited Er during the sputter-deposition on the processing temperature window for ErSi$_2$ formation can be explained as follows: (a) ErSi$_2$ nucleation barrier increases with the presence of oxygen in the amorphous Er/Si(O) interlayer; (b) oxygen diffuses from the top Er oxide layer, through the unreacted Er layer, into the Er/Si(O) interlayer and becomes saturation quickly even before ErSi$_2$ nucleation at high
processing temperatures; (c) the incorporated oxygen influences on the microstructure of as-deposited Er and thus affect on the oxygen diffusion through the unreacted Er layer.

Using a Ti capping layer after the sputtering deposition of Er film is proposed as a possible solution to the oxygen contamination. Ti capping layer has been demonstrated to have a beneficial influence on the erbium silicide films: (1) it broadens the process window of ErSi$_2$ formation both by decreasing the minimum temperature required for ErSi$_2$ formation and, more substantially, by increasing the maximum allowable temperature and (2) it also improves the film quality. This beneficial effect of Ti capping is attributed to the suppressed incorporation of the oxygen in the bulk of Er film from the annealing ambient (Ti readily reacts with oxygen) during the RTA silicidation as well as the oxygen-gettering ability (to getter already incorporated oxygen in Er) of Ti due to its chemical activity. However, we are not clear about the exact reason at the moment. Future work will be performed to explore the cause for Ti to reduce the defects.

6.2 Suggestions for future work

To obtain consistent results and to further confirm the overall understanding, repeated measurements and thorough analyses combined with continuous works need to be carried out. It is encouraged to prepare the samples in an ultra high vacuum chamber, to ensure oxide-free interface and surface, and also to confirm that the
structural defects are indeed not caused by oxidation.

Surface morphology of silicides is not fully understood, in particular related to the effect of Ti capping on the formation of structural defects. To study this, the use of characterization technique using TEM is strongly encouraged. Using this technique, the surface defects can be investigated more thoroughly.

To have a better understanding of the feasibility of the capping layer, it is suggested to use other kind of films such as TiN, W to prevent the oxygen diffusion during RTA process. Using vacuum ambient during the RTA is another preferable way to get ErSi$_2$ film.