

**THE OXIDATION KINETICS AND INTERFACE
STABILITY OF SILICON (Si) AND
COBALTDISILICIDE (CoSi_2) IN DRY THERMAL
OXIDATION**

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of the Requirement for the Degree
of Master of Science in Physics

By

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ABSTRACT

Oxidation kinetics and interface stability of Si, surface and buried CoSi_2 have been studied in temperature range of 1000-1150 °C in dry oxygen ambient. Measurement of the thickness of SiO_2 formed by the oxidation of Si, surface and buried CoSi_2 show a linear-parabolic behavior in time. The Characterization was performed by Rutherford backscattering spectrometry (RBS) and Ionchanneling of 1.4 MeV He^+ ion, Van der Pauw resistivity measurement, ellipsometry and cross-sectional transmission electron microscopy (X-TEM) for micro-structural analysis. The comparison of oxidation rates of Si with surface and buried CoSi_2 is performed and it was found that the rate is higher for surface CoSi_2 for temperatures 1000 °C, 1050 °C and 1100 °C and the rate for Si is higher for 1150 °C but the rate of Si and buried CoSi_2 are found to be the same for 1150°C.

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1. INTRODUCTION

The oxidation of silicon(Si) is necessary during the entire process of fabricating modern integrated circuits. The production of high-quality integrated circuits (ICS) requires not only an understanding of the basic oxidation mechanism, but the ability to form, in a controlled and repeatable manner, a high-quality oxide. In addition to ensure the reliability of the ICS, the electrical properties of the oxide must be understood [1,2].

However, the advent of very-large scale integration in microelectronics has placed severe demands upon interconnection technology. The practices of using polycrystalline silicon or diffusions for the interconnect material is no longer feasible because of the high resistance involved when scaling down. The most important desired properties of an interconnect material are low resistivity and the possibility to form electrically insulating thermal oxide. Because of its excellent conductivity and ability to form thermal oxide, cobalt disilicide (CoSi_2), which has already proved to be very suitable as ohmic or rectifying contacts, is now gaining favor as an interconnect material. For such applications it is necessary to cover the CoSi_2 with an insulating layer, such as SiO_2 , to enable the use of over crossing conductors in subsequent layers. For this reason the oxidation of the metal CoSi_2 and its stability during oxidation is of great interest [3,4,5,6,7].

Silicon dioxide has several uses: to provide isolation between devices, to mask against impurities, dopant diffusion, and environmental effects; to provide stability against mechanical damages, e.g., scratching; to act as an insulating layer between conductors and to act as the gate dielectric. Basically, the SiO_2 layers can be used in the ways described above successfully [1,2].

Several techniques for forming the SiO_2 layer have been developed such as, thermal oxidation, wet anodization, vapor phase technique [chemical vapor deposition (CVD)], and plasma anodization or oxidation, either in dry or wet oxygen ambient. In our work, we used dry thermal oxidation technique using rapid thermal annealer (RTA) in dry oxygen ambient.

This topic has been a continuing subject of many investigations as shown in the published articles in the past years [1-16]. However, oxidation kinetics and interface stability after high temperature oxidation of surface CoSi_2 have not yet been reported.

In this thesis the fabrication of SiO_2 over Si, surface CoSi_2 and buried CoSi_2 , its characterization to study the kinetics i.e, thickness dependence on oxidation temperature and time of thermal oxidation of Si, surface CoSi_2 , buried CoSi_2 and their oxidation rate comparison over (100) Si substrate are reported. The Deal-Grove oxidation model is used to fit the obtained experimental data.

A variety of analytical techniques have been employed to characterize the oxidation products and to measure SiO_2 thickness. Rutherford backscattering spectrometry (RBS) has been used most frequently. Other techniques are ellipsometry, Van der Pauw resistivity measurement and transmission electron microscopy (TEM). The new results that have never been reported i.e., the formed SiO_2 thickness versus short oxidation time for different temperatures and its structural stability at 1100°C and 1150 °C for both surface and buried CoSi_2 . X-TEM were used for microstructural and interface analysis. The comparison of oxidation of Si with surface CoSi_2 and si with buried CoSi_2 were performed.

2. CHARACTERISATION TECHNIQUE

2.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford backscattering is a widely used analysis technique in many branches of material science. The basic concepts of Rutherford backscattering (RBS) are: A Beam of energetic ions is directed at the solid under investigation. The ions collide elastically with lattice atoms within the sample and are scattered back into a suitable detector that counts the number of scattered particles and measures their energy. The information contained in the scattered particles can be interpreted to give data on the composition of the sample, the distribution of components within a sample and the sample thickness. Backscattering rests on two basic process: the large scattering angle of two colliding nuclei and the energy loss incurred by swift particles in a medium. Consider a light particle of mass m and energy E impinging on stationary heavy particle of mass M (see Fig 2.1).

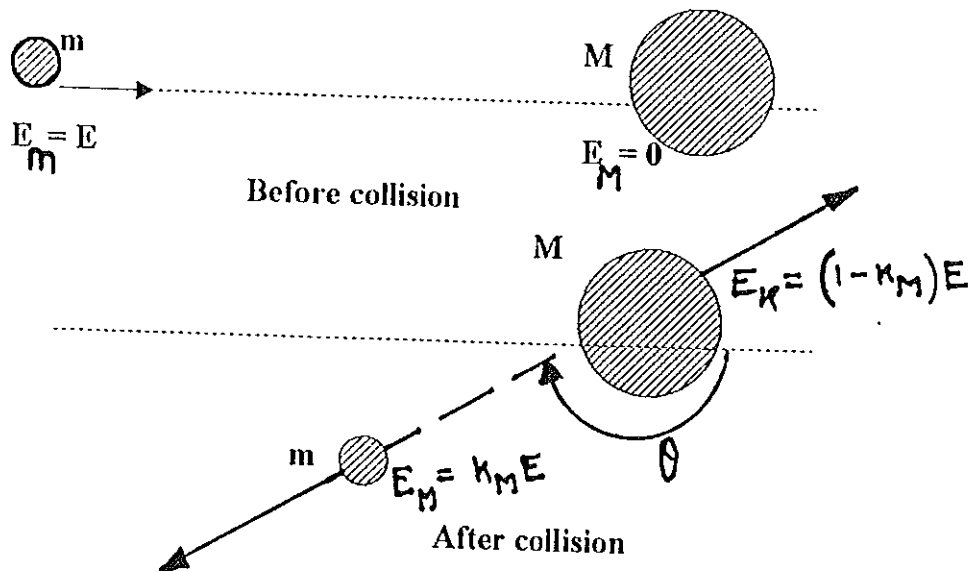


Fig.2.1 Schematic representation of an elastic large angle collision of a swift light particle of mass m with a stationary heavy mass M .

If the two particles undergo an elastic collision and the light mass is deflected by an angle θ from its original direction of motion, the light mass will have a residual energy $K_M E$ that is

less than its original energy, i.e., $K_M < 1$. The value of K_M follows from the conservation of energy and momentum [30]:

$$K_M = \left[\frac{\left(M^2 - m^2 \sin^2 \theta \right)^{\frac{1}{2}} + m \cos \theta}{M + m} \right]^2 \quad (2.1)$$

The kinematic factor K_M does not depend on the energy E before the collision; the fraction of energy retained by the light particle after collisions is the same for any initial energy value E . The fraction depends explicitly on the angle of deflection θ . For $\theta = \pi$ the value of K_M has its lowest value, which is

$$K_M = \left[\frac{M - m}{M + m} \right]^2, \theta = 180^\circ \quad (2.2)$$

In backscattering spectrometry, as the name indicates θ is almost always close to 180° .

In backscattering, the light mass in this model stands for the particle of the analyzing beam (usually He^+ ion). The heavy mass M represents an atom in the sample to be analyzed.

Particles that are scattered at angle θ , into a solid state detector that subtends a solid angle that is small. The number of counts, Y registered by the detector is given by

$$Y = QNt \frac{d\sigma}{d\Omega} \quad (2.3)$$

where Q is the number of particles that strike the target, N is the volume density of target atoms, t is the target thickness $d\sigma/d\Omega$ is the average differential scattering cross-section for scattering into a solid angle at a scattering angle θ . For small values of Ω the average $\langle d\sigma/d\Omega \rangle$ can be approximated by the differential scattering cross-section $d\sigma/d\Omega$ and this

is usually referred to simply as the scattering cross-section and given the symbol σ . Thus the yield can be written as:

$$Y = QNt\sigma\Omega \quad (2.4)$$

If the number of particles striking the target and detector are counted and are both known then the number of atoms per unit cross-sectional area of the target, i.e., Nt can be determined. Large-angle scattering collisions being highly unlikely, the rate of average particles moving swiftly through a medium is controlled by other energy-loss interactions, termed dE/dX losses. The name refers to the transmission experiment sketched in Fig. 2.2, to measure this loss. As the thickness ΔX of the target approaches sufficiently small values the energy ΔE lost by the particles in transit through the target is proportional to ΔX and one defines

$$\lim_{\Delta X \rightarrow 0} \frac{\Delta E}{\Delta X} = \frac{dE}{dX}(E) \quad (2.5)$$

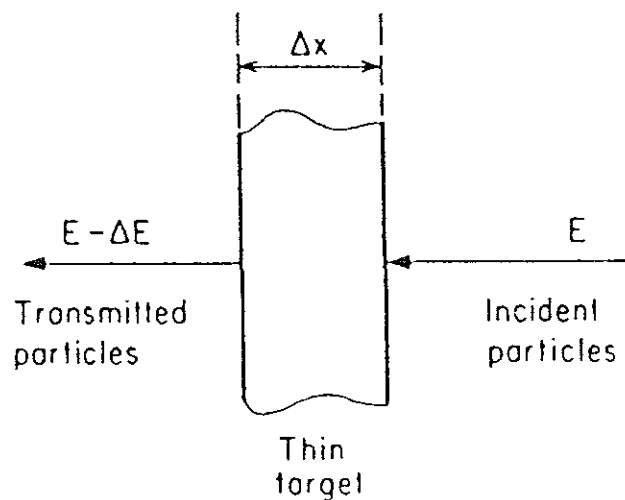


Fig 2.2 Schematic representation of a transmission experiment to determine the dE/dX loss of a swift particle moving through a medium.

For that particle and energy in that medium. The thickness X is assumed to be quite small, and in the limit, one defines

$$\epsilon = \left(\frac{1}{N} \right) \lim_{\Delta X \rightarrow 0} \frac{\Delta E}{\Delta X} = \frac{1}{N} \frac{dE}{dX}(E) \quad (2.6)$$

As the stopping cross section.

For light projectile atoms and energy range of interest to backscattering spectrometry, the two dominant processes of energy loss are the interactions of the moving in with the screened or unscreened nuclei of the target atoms. One thus sets

$$\epsilon = \epsilon_e + \epsilon_n \quad (2.7)$$

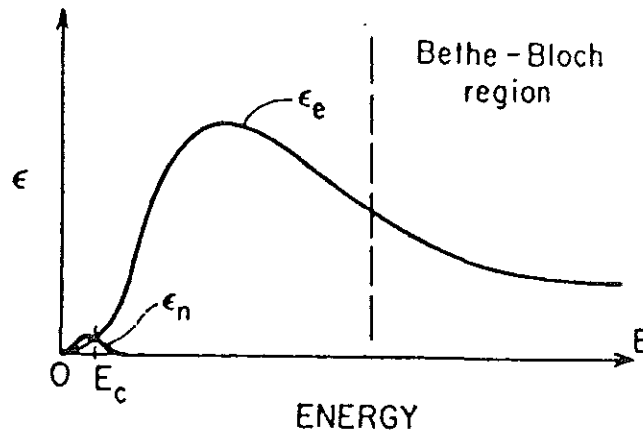


Fig.2.3 Dependencies of electronic ϵ_e and nuclear ϵ_n contributions to the Stopping crosssection as a function of the incident particle energy E [30].

E_c is the energy at which nuclear and electronic ϵ are equal.

In this work a brief introduction into RBS, is given. For further information the reader is referred to [23,30,31]. However the advantages of this technique are obvious the ability to perceive depth information, qualitative and quantitative, without serious destruction. On the

other hand one should mention that chemical information is totally absent and any non uniformities e.g.. cavities, scratches or dust particles can drastically modify the spectrum. All in all RBs should be considered as one of a number of different investigation techniques like (TEM, SIMS, SEM, AES and Ellipsometry) with its strength and weakness. As the SiO_2 thickness is merely a few hundred angstroms in the linear regime, careful experimental procedure, accurate thickness measurement and a large number of data are necessary in order to obtain a reliable linear rate constant. The accuracy of RBS usually about 30 Å [4].

2.2 Channeling

Ion channeling is often used in conjunction with RBS. The channeling phenomenon will be briefly described here. When the incident direction of an ion beam is aligned with a crystallographic axis or plane of single crystal sample the majority of the ions penetrate (channel) into the crystal, channeled particles cannot get close enough to the atomic nucleus to undergo large angle Rutherford scattering and hence the backscattering is drastically reduced. The channeling phenomenon and an RBS spectrum under channeling condition are schematically shown in Fig. 2.5 and Fig. 2.6 respectively.

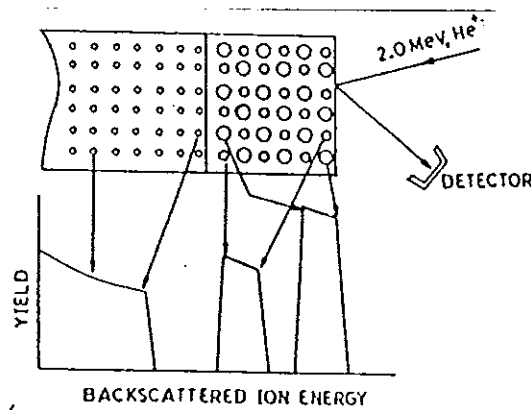


Fig. 2.4 Schematic diagram of a typical backscattering spectrum of thin film containing two different masses on a low atomic number (Z) elemental substrate [32].

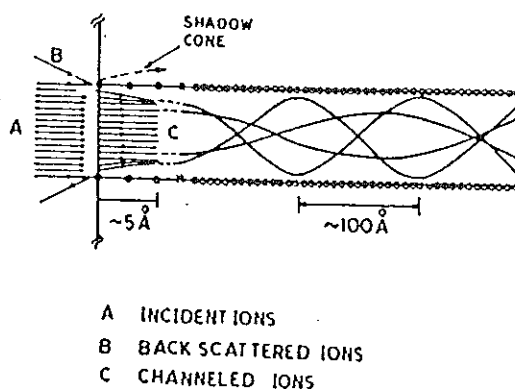


Fig 2.5 Schematic representation showing trajectories of particles undergoing scattering at the surface and channeling within the crystal. The shadow cone¹ is also shown in dotted lines. The depth scale is compressed relative to the width of the channel in order to display the shape of the trajectories [23].

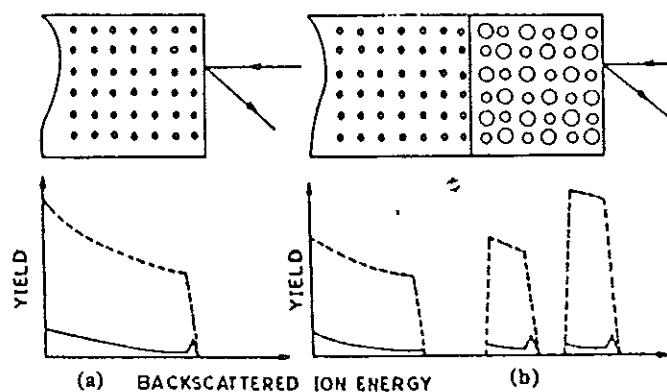


Fig. 2.6 Schematic backscattering spectrum (a) mono elemental crystal substrate and (b) crystalline thin film (compound) on this substrate under channeling (solid lines). The dashed lines show the backscattering spectrum for random incidence [32].

In fact, the channeling effect is observed within an angular range which depends on the type of ion, the incident energy of the ion, the type of the sample crystal and its specific crystallographic axis or plane along which the beam is incident, and finally on the thermal vibrational amplitude of the constituent atoms in the sample crystal. This angular range is expressed in terms of a critical angle (or half-angle) $\Psi_{1/2}$ given by [32]

¹ Shadow cone is the screening effect of the interaction potential of the two scattering particles.

$$\Psi_{\frac{1}{2}} = \frac{2Z_1 Z_2 e^2}{Ed} \quad (2.8)$$

where d is the atom spacing along the row, Z_1 is the nuclear charge of the incident particle and E is an energy of incident particles in Mev. For atomic rows containing more than one type of atoms or uneven spacing, Z_2 and d are interpreted as an average nuclear charge or an average atomic spacing.

The ratio of the backscattering yield for the channeled condition to that for the random incidence is denoted by $\chi_{\min}$ and called the minimum yield. It is a measure of the crystalline quality of the sample.

$$\chi_{\min} = N_a d \pi (2U_1 + a^2) \quad (2.9)$$

where N_a is the no. of atoms/ A^3 , U_1 is the atomic vibrational amplitude and a is Thoms-Fermi screening radius given by

$$a = \frac{0.4685}{\left(Z_1^{1/2} + Z_2^{1/2}\right)^{2/3}} \quad (2.10)$$

For a good crystal at room temperature $\chi_{\min}$ is typically a few percent [30,31,32]. This drastic reduction in the backscattering under the channeling condition improves the ion scattering sensitivity to light impurities on the surface.

Thus, the combination of RBS and channeling can be used to measure the degree of crystal perfection in a given target and to locate the position of foreign impurities within target lattice.

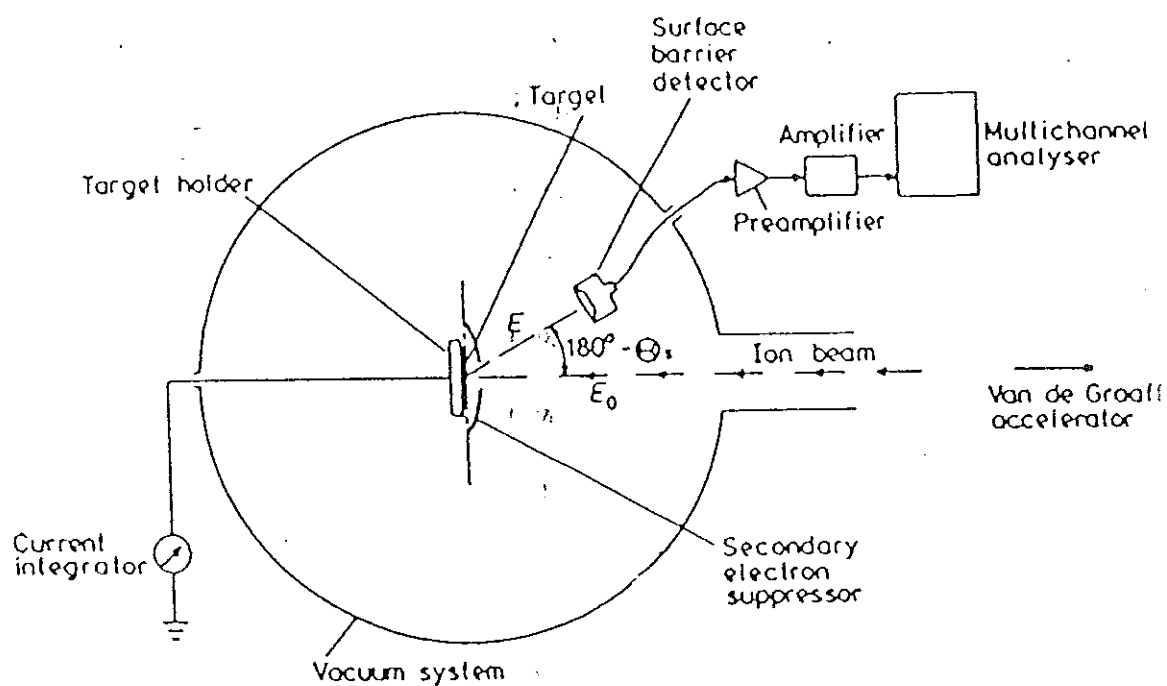


Fig. 2.7 Schematic of Rutherford backscattering chamber and electronics for energy analysis of the scattered particles.

2.3 Van der Pauw Resistivity Measurement

The resistivity can be measured in a number of ways. The methods range from contactless, through temporary contact to permanent contact techniques. Van der Pauw method is one of the ways; He showed how the specific resistivity of a flat sample of arbitrary shape can be measured without knowing the current pattern, if the following conditions are met [31,33]:

(1) the contacts are at the circumference of the sample (2) the contacts are sufficiently small, (3) the sample is uniformly thick, and (4) the surface of the sample is singly connected, i.e., the sample does not contain any isolated holes.

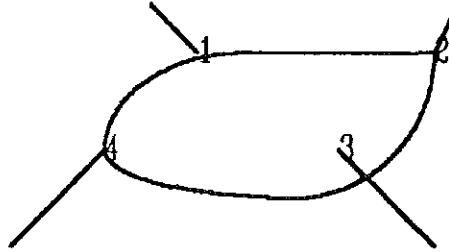


Fig. 2.8 Arbitrarily shaped sample with four contacts.

Consider a flat sample of a conducting material of arbitrary shape, with contacts 1, 2, 3 and 4 along the periphery as shown in Fig. 2.8 to satisfy the conditions above. The resistance $R_{12,34}$ is defined as

$$R_{12/34} = \frac{V_{34}}{I_{12}} \quad (2.11)$$

where the current I_{12} enters the sample through contact 1 and leaves through contact 2 and $V_{34} = V_3 - V_4$ is the voltage difference between the contact 3 and 4. $R_{23,41}$ is defined similarly. The resistivity is given by

$$\rho = \frac{\pi t}{\ln(2)} \frac{(R_{12/34} + R_{23/41})F}{2} \quad (2.12)$$

where F is a function of only the ratio

$$R_r = R_{12/34}/R_{23/41}$$

$$\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln(2)} \arccos h\left(\frac{\exp[\ln(2)/F]}{2}\right) \quad (2.13)$$

and t is thickness of the sample. The function F on the right side of Eq.(2.12) depends only on R_r . For a symmetrical sample such as a circle or a square, $R_r = 1$ and $F = 1$. This allows Eq.(2.12) to be simplified to

$$\rho = \frac{\pi t}{\ln(2)} R_{12/34} = 4.532tR_{12/34} \quad (2.14)$$

The sheet resistance is given by

$$\rho_s = \frac{\pi}{\ln(2)} R_{12/34} = 4.532R_{12/34} \quad (2.15)$$

The Van der Pauw equations are based on the assumption of negligibly small contacts located on the sample periphery. Real contacts have finite dimensions and may not be exactly on the periphery of the sample. To avoid the error caused by non-ideal contacts and complicated sample preparation; square samples are generally used. One of the advantages

of the Van der Pauw structure is the small sample size compared with the area required for other measurements. Van der Pauw structures are therefore preferred for integrated circuit technology.

2.4 Ellipsometry

Ellipsometry is used predominantly to measure the thickness of a thin dielectric films on highly absorbing substrates. It allows thickness measurements at least an order of magnitude smaller than interferometric methods. Ellipsometry is based on measuring the state of polarization of polarized light.

The ellipsometric angles Ψ ($0^\circ \leq \Psi \leq 90^\circ$) and Δ ($0^\circ \leq \Delta \leq 360^\circ$) are the most commonly used variables in ellipsometry and are defined as

$$\Psi = \tan^{-1} \left(\frac{R_p}{R_s} \right) \quad (2.17)$$

$$\Delta = \Delta_p - \Delta_s \quad (2.18)$$

Where R_p and R_s are parallel and perpendicular component of reflection coefficient respectively.

Ψ and Δ determine the differential changes in amplitude and phase, respectively, experienced upon reflection by the components of the vibrations of the electric field vectors parallel and perpendicular to the plane of incidence.

The major application of ellipsometry is for measurements of thickness and index of refraction of thin, non-absorbing films on semiconductor substrates. There is, in principle,

no limit to the thickness of the layer that can be determined. Films as thin as 10 Å have been measured, as have films many thousands of Angstroms thick [31]. The model assumes uniform optical properties and a sharp planar film/substrate boundary. Furthermore the ellipsometric equations are based on the macroscopic Maxwell's equations that generally do not apply to layers only a few atomic layers thick. Nevertheless, the measurements appear to give reasonable average thicknesses.

Thick layers have a different problem. The interpretation becomes more difficult due to optical path lengths. In Fig. 2.9 we show a thin transparent layer on a substrate. The two reflected rays interfere with one another, ranging from being completely in phase to being completely out of phase. A consequence of this interference is the cyclical nature of thickness measurements. Where ψ and Δ are cyclic functions of the film thickness. They repeat for the full - cycle film thickness.

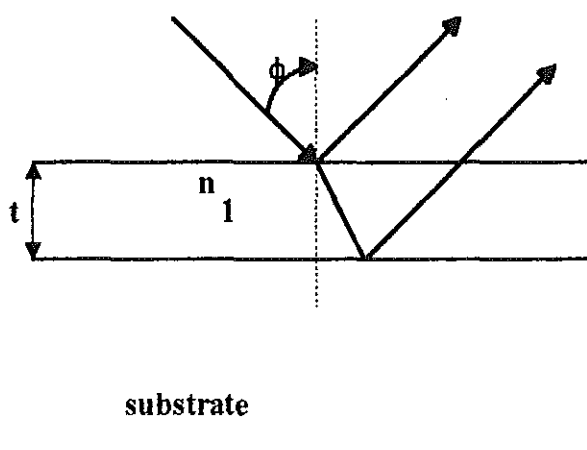


Fig. 2.9 Schematic showing multiple reflections.

$$t = \frac{\lambda}{2(n_1^2 - \sin^2(\phi))^{1/2}} \quad (2.19)$$

Where t is a film thickness, n_1 is the refractive index of a film and ϕ is an angle of incidence.

For example, at $\phi = 70^\circ$ the full-cycle thickness of SiO_2 films with $n_1 = 1.465$ at $\lambda = 0.6328 \mu\text{m}$ is 2815 Å. If a 500 Å thick SiO_2 film gives certain ellipsometric angles, the same angles will be measured for films $(500 + 2815)\text{Å}$, $(500 + 5630)\text{Å}$, etc. Hence for films thicker than the full-cycle thickness, one must have independent knowledge of the film thickness to within the full-cycle thickness. Ellipsometry, offering a sensitivity of 1 Å, might be adequate thickness measuring technique, although it requires accurate refractive index values for the silicide and the SiO_2 film grown on the silicide.

3. REVIEW OF OXIDATION OF Si AND CoSi₂

3.1 Growth Mechanism of SiO₂ over Si substrate

Since a silicon surface has a high affinity of oxygen, an SiO₂ layer rapidly forms when it is exposed to an oxidizing ambient. The chemical reaction describing the thermal oxidation of silicon in dry oxygen ambient is given in E.q. (3.1).



The basic process involves shared valence electrons between silicon and oxygen; the silicon-oxygen bond structure is covalent. During the course of the oxidation process the Si-SiO₂ interface moves into the silicon; however, the volume expands, resulting in the external SiO₂ surface not being coplanar with the original silicon.

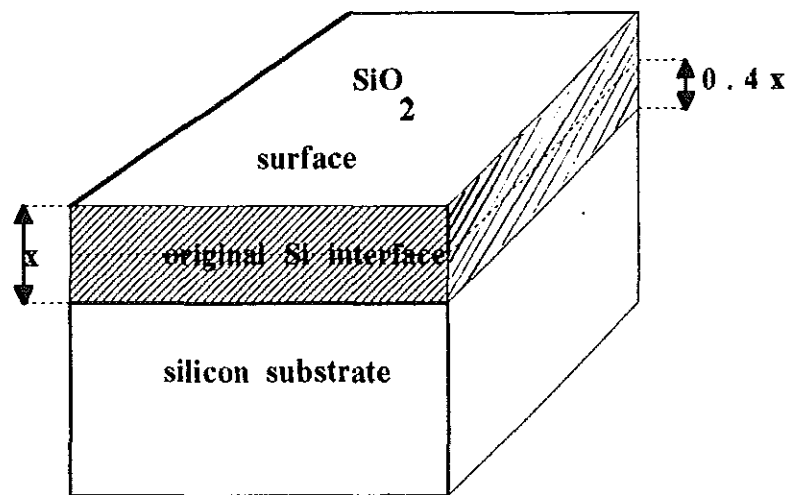


Fig. 3.1 Growth of SiO₂.

In growing SiO₂ from Si, due to the changes in density and molecular weight a film of SiO₂ with a thickness of X consumes a layer of crystalline Si about 0.45 X [1] in thickness; the SiO₂-Si interface is therefore displaced from the original Si surface and located deep into the

Si wafer. It has also been observed that for oxidation in dry oxygen ambient, the oxidising species move through the SiO_2 layer to react with Si. The main effect of a displaced and deeper interface and of an inward migration of the oxidizing species through the SiO_2 layer is to provide a clean- SiO_2 interface, free of contaminants due to air exposure prior to oxidation (inter-facial impurities tend to end up on the SiO_2 surface).

3.2 Major Process in the Growth of SiO_2 over CoSi_2

As shown in Fig. 3.2, the oxidation process can be separated into four steps [4,6,8]:

- (1) diffusion of the oxygen-molecules through the SiO_2 layer,
- (2) reaction at the CoSi_2 - SiO_2 interface
- (3) net transport of silicon atoms relative to the cobalt atoms in the CoSi_2 ,
- (4) reaction at the silicon- CoSi_2 interface that releases silicon from the substrate.

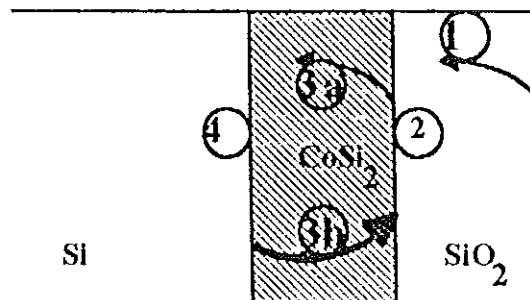


Fig. 3.2 The four major steps in the oxidation process.

Let us state the conditions for the two limiting cases in oxidation: Reaction controlled and diffusion controlled oxidation occurs when $D \gg K_r X_o$ and $D \ll K_r X_o$ respectively, where D is the diffusivity, K_r is the chemical reaction rate for oxidation at interface and X_o thickness of SiO_2 at a given time.

Step (1) is the only diffusion-controlled process that would yield a parabolic time dependence of the SiO_2 thickness is the transport of the oxidizing species through the growing SiO_2 . We adopt the Deal-Grove (linear-parabolic) oxidation model [9]. The model will be described in section 3.5.

$$X^2 + AX = B(t + \tau) \quad (3.2)$$

where X is the SiO_2 thickness, t is the oxidation time, B is the parabolic rate constant, B/A is the linear rate constant and τ is a shift in time co-ordinate which corrects for the presence of the initial SiO_2 layer. Thus the observed linear- parabolic growth kinetics of CoSi_2 oxidation indicates that this step is the rate limiting process in the parabolic regime of oxidation [4,6]. Step (2) it is not yet explored very well but it can be explained in terms of thermodynamics. The chemical equilibrium reaction at this interface, assuming all oxygen at this interface is reacted, and unlimited supply of Si from the substrate; CoSi_2 will grow a SiO_2 layer [6]. The prediction from thermodynamic analysis that is H_R is negative [6,8]. Where H_R is the heat of reaction. The thermodynamic analysis attempts to predict only the SiO_2 or cobalt oxide that may form. The chemical reactions at that interface are not considered. These unexplored reaction rate are a factor in the linear rate constant B/A .

Step (3) the Si transport (relative to the cobalt atoms in the CoSi_2) during oxidation is a second factor that affects A . In the case of CoSi_2 , there are two possible cases;

- (i) silicon is supplied from the substrate and diffuses through the CoSi_2 to the SiO_2 interface
- (ii) the CoSi_2 dissociates at the CoSi_2 - SiO_2 interface and the cobalt atoms diffuse through the CoSi_2 to silicon substrate, where it reacts again

with silicon and reforming the CoSi_2 that keeps the CoSi_2 layer unchanged during oxidation.

Step (4) reaction at the Si-CoSi_2 interface during oxidation is similar in nature to the reaction at the interface during CoSi_2 formation. CoSi_2 formation is usually diffusion controlled not reaction controlled at low temperatures at which the reaction can be analyzed. The rates of Si consumption, however, are roughly the same in both oxidation experiments performed at high temperatures and CoSi_2 formation experiments at low temperatures. Because at those rates the reaction at the Si-CoSi_2 interface is fast, it must be negligible also at high temperature oxidation as a rate limiting process. Generally, for oxidation of CoSi_2 for high temperature oxidation steps 2,3 and 4 are not rate limiting in the parabolic regime but rather they are rate limiting in the linear regime.

3.3 Transport Process in the Growth of SiO_2 over CoSi_2 Film

As the SiO_2 layer grows, there is necessarily an overall displacement of Si with respect to the cobalt. To see that, consider for example the top interface of the CoSi_2 . Before oxidation there is no Si above that interface, but after oxidation Si (in formation of SiO_2) resides on top of the CoSi_2 . The question addressed here is; how does this displacement of one specie against the other take place? To answer this question an Inert Marker experiment is performed, this experiment confirms CoSi_2 remains stoichiometric during oxidation.

It is through the decomposition of CoSi_2 [7] that the formation of SiO_2 over CoSi_2 occurs and maintaining the CoSi_2 layer during oxidation process occurs through the reverse diffusion of the dissociated cobalt atoms to the inner silicon- CoSi_2 interface[7]. This is proved by Inert Mark experiment [3,7]. An inert marker (evaporated tungsten or ion

implanted xenon) is used to investigate the oxidation process of CoSi_2 layer. This inert marker does not change position during oxidation of CoSi_2 in back scattering energy space as described in fig. 3.3.

This experiment gives the first hand evidence about the dissociation of CoSi_2 and the inward diffusion of cobalt atoms toward the silicon substrate and the formation of CoSi_2 layer again. But for higher temperature (1150°C) there is a possibility that the silicon from the substrate diffuses through CoSi_2 layer and can supply Si to the formation of SiO_2 layer over the CoSi_2 layer. Hence, there are two possible transport mechanism that supply Si to the formation of SiO_2 layer in the oxidation of CoSi_2 .

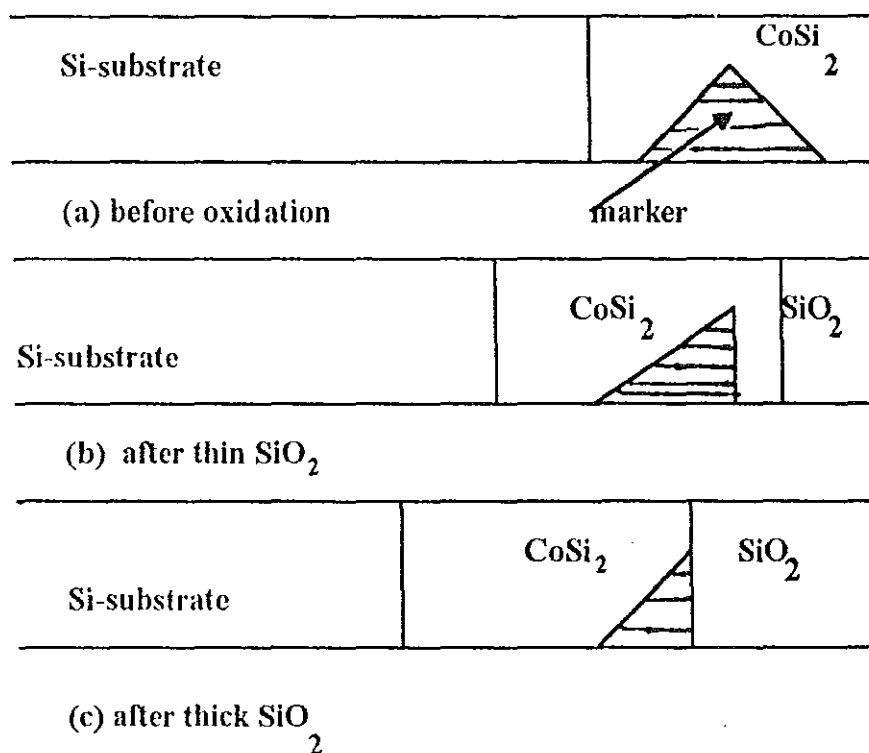


Fig.3 3 Marker position for CoSi_2 oxidation.

3.4 Properties of SiO_2

Thermally grown SiO_2 films are amorphous. They consist of a random three-dimensional network of silicon atoms tetrahedrally surrounded by four oxygen bridges at the corners, as shown in the two-dimensional network shown in fig. 3.4.

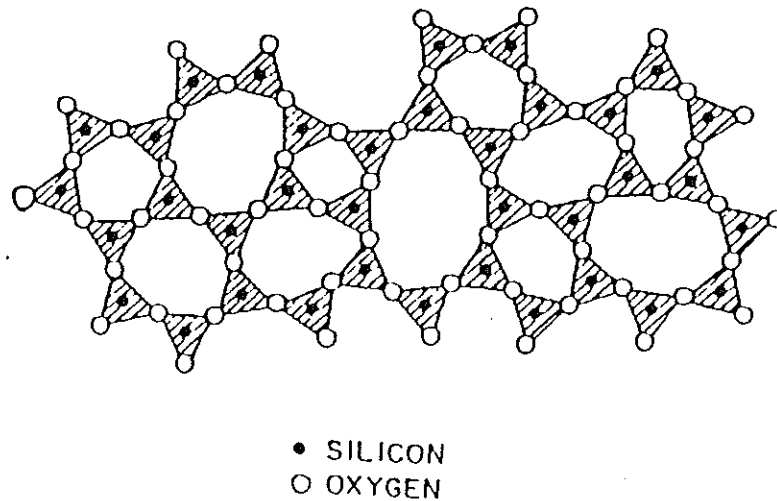


Fig. 3.4 Two-dimensional Schematic Representation of the Amorphous Structure of Fused Silica.

As is apparent, this type of structure has open space. This is also reflected in the low density of the amorphous SiO_2 compared to that of crystalline SiO_2 (2.27 g.cm^{-3} versus 2.65 g.cm^{-3}). In fact, only 43% [2] of the total measured volume is occupied by SiO_2 molecules. In spite of this open structure, SiO_2 films are excellent barriers to the diffusion of several dopants and metals. The diffusivity of O_2 in SiO_2 can be calculated by using the Arrhenius equation:

$$D = D_0 \exp(Q/kT) \quad (3.3)$$

Where D is the diffusivity at temperature T , D_0 is the diffusivity constant, Q is the activation energy, k is Boltzmann's constant, T is the absolute temperature. Let X be the diffusion

depth in time t then the relation between X and t is given by:

$$X^2 = 4Dt \quad (3.4)$$

The diffusivity of O_2 is high and it is very essential. During thermal oxidation; these Oxidising species diffuse rapidly through the oxide layer growing on the silicon and continue to react with Silicon at the Silicon-oxide interface. If the diffusivity of O_2 in SiO_2 were low, the SiO_2 formed at the initial stages of oxidation would have been self limited.

SiO_2 films on Silicon are very successfully used as diffusion barriers (or masks) for dopants since dopants have very low diffusivities in SiO_2 . Oxide films are used as masks to prevent ion implantation in chosen regions of the silicon.

Capacitance-voltage (C-V) characteristics of the Metal-oxide-semiconductor (MOS) capacitor have provided real insight into the electronic structure of the SiO_2 and the semiconductor. They allow us to create pictorially the effect of applied bias on the bending of the semiconductor energy bands inside the semiconductor. Ideally, the SiO_2 film should truly be an insulator; it should have infinite resistivity, which ranges from 10^{14} to $10^{16} \Omega\text{cm}$ [1] at 25°C . Contamination can lower the resistivity. Noticeable conduction has been observed in the SiO_2 with electric fields as small as $1-2 \times 10^6 \text{ V/cm}$ [1,2] across the oxide.

The quality of the thermally grown SiO_2 (or any other insulator) is normally characterized by measuring the so-called dielectric or breakdown strength of the film. Normally, a large number of capacitors, fabricated directly on the SiO_2 , are subjected to increasing DC bias across the insulator and the current is measured. Capacitors that pass more current than the present amount, usually $1-2 \mu\text{amps}$. [2] are considered to be failed. Some of the properties of thermally grown silicon dioxide are listed in Table I.

Table I Properties of Thermal Silicon Dioxide

DC resistivity ($\Omega \cdot \text{cm}$), 25°C	$10^{14} - 10^{16}$
Density (g/cm^3)	2.27
Dielectric Constant	3.8 - 3.9
Dielectric Strength (V/cm)	$5-10 \times 10^6$
Energy gap (eV)	~ 8
Etch rate in buffered HF (nm/min)*	100
Infrared absorption peak (μm)	9.3
Linear expansion Coefficient ($/^{\circ}\text{C}$)	5.0×10^{-7}
Melting Point ($^{\circ}\text{C}$)	~ 1700
Molecular Weight	60.08
Molecules/ cm^3	2.3×10^{22}
Refractive index($\lambda = 0.6328 \mu\text{m}$)	1.46
Specific heat ($\text{J/g} \cdot ^{\circ}\text{C}$)	1.0
Stress in film on Si (N/m^2)	2.4×10^8
Thermal Conductivity ($\text{W/cm} \cdot ^{\circ}\text{C}$)	0.014

(Source: Wolt and Tauber (1986))

* Buffered Hydrofluoric acid (HF): 28 ml HF, 170 ml H_2O . 113 g Ammonium
Fluoride (NH_4F).

3.5 Kinetics

Deal and Grove's model describes the Kinetics of Silicon oxidation. The oxidation model proposed by Deal and Grove (1965) [19] is shown schematically in Fig. 3.5. According to this model, for the oxidizing species to reach the silicon surface, there are steps in series:

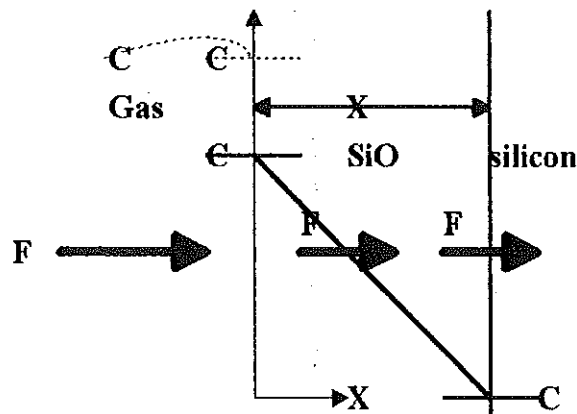


Fig. 3.5 Model for the Thermal Oxidation of Silicon. Direction of gas flow is normal to plane of paper. [19]

1. The oxidizing species must be transported from the bulk of the gas to the SiO_2 -gas interface. The flux is given by:

$$F_1 = h_G(C_G - C_s) \quad (3.5)$$

Where h_G is the mass-transfer coefficient and C_G and C_s are the concentration of the oxidant in the bulk of the gas and in the gas at the SiO_2 surface, respectively. We now want to relate the concentrations of the oxidant in the gas to the concentrations of the oxidant in the solid (SiO_2) through Henry's law[18]. The idea behind Henry's law is that the equilibrium concentration of a species in a solid is proportional to the partial pressure of that species in the surrounding gas. To apply Henry's law to the given situation, the concentration of the oxidant at the oxide surface (but within the oxide) is

$$C_o = K_H P_S \quad (3.6)$$

where C_o is the actual concentration of the oxidant at the oxide surface (within the oxide), K_H the Henry's law constant, and P , the partial pressure of the oxidant at the oxide surface (within the oxide), C^* is the equilibrium concentration of the oxidant with in oxide, that would be in equilibrium with the partial pressure in the bulk of the gas P_G is given by:

$$C^* = K_H P_S \quad (3.7)$$

the driving force for F_1 is therefore proportional to the deviation from equilibrium (i.e. $C^* - C_o$). Using the ideal gas law,

$$PV = N_M KT \quad (3.8)$$

the gas-phase oxidant concentrations can be expressed as;

$$C = \frac{N_M}{V} = \frac{P}{kT} \quad (3.9)$$

where P is the partial pressure of the oxidant in the gas, N_m the number of molecules of the oxidant in the gas, and C the gas-phase concentration expressed in units of molecules/volume. The concentration of oxidant in the bulk of the gas C_G is

$$C_G = \frac{P_G}{KT} \quad (3.10)$$

and the concentration of the oxidant at the oxide surface (but in the gas)

$$C_s = \frac{P_s}{KT} \quad (3.11)$$

substituting into eq.(3.5) yields

$$F_1 = h_O(C_O - C_s) = \frac{h_O(P_O - P_s)}{KT}$$

using equations. (3.6) and (3.7), F_1 can be expressed as

$$F_1 = \frac{h_O(P_O - P_s)}{KT} = h(C^* - C_o) \quad (3.12)$$

where

$$h = \frac{h_O}{KTK_H}$$

2. The oxidizing species must diffuse across the oxide layer already present. The diffusional flux F_2 is given by

$$F_2 = D \frac{(C_o - C_i)}{X_o} \quad (3.13)$$

where D is the diffusivity, C_i the concentration of the oxidant at the oxide - Si interface, and X_o is the thickness of the oxide at a given time, t .

3. The oxidizing species must then react with the Si at the oxide-Si interface. The flux to incorporate the oxidant into Si, F_3 is given by;

$$F_3 = K_S C_i \quad (3.14)$$

where K_s is the chemical reaction rate constant for oxidation at the oxide-Si interface. These three steps are in series; the slowest step among the three will control the entire process of oxidation. When a steady-state condition is established, all fluxes are equal (i.e. $F = F_1 = F_2 = F_3$). Solving for C_i and C_o , we have;

$$C_i = \frac{C^*}{(1 + K_s/h + K_s X_o/D)} \quad (3.15)$$

and

$$C_o = \frac{(1 + K_s X_o/D)C^*}{1 + K_s/h + K_s X_o/D} \quad (3.16)$$

In thermal oxidation of Si, step 1(F_1) is rarely the rate limiting step [19]. We can assume that h is much larger than K_s . With this assumption eqs. (3.15) and (3.16) can be further simplified to

$$C_i \cong \frac{C^*}{1 + K_s X_o(t)/D} \quad (3.17)$$

and

$$C_o \cong C^* \quad (3.18)$$

Let us consider the situation where step 2(F_2) is the rate - limiting step. For this to occur, the diffusivity of the oxidizing species, D , is very small compared to $K_s X_o(t)$, thus causing $C \rightarrow 0$. This is the case where the oxidation process is said to be diffusion controlled. In the opposite case where D is very large compared to $K_s X_o(t)$, $C_i \rightarrow C^* \sim C_o$. The oxidation is said to be interfacial reaction controlled. Combining eqs. (3.15), (3.16),

and (3.17) and eliminating C_p , the flux F is given by

$$F = \frac{DC_oK_s}{D + K_sX_o} \quad (3.19)$$

Thus the rate at which the oxide layer grows is

$$\frac{dX_o}{dt} = \frac{F}{N} = \frac{DC_oK_s}{N} \frac{1}{D + K_sX_o} \quad (3.20)$$

where N is the number of oxidant molecules incorporated into a unit volume of oxide.

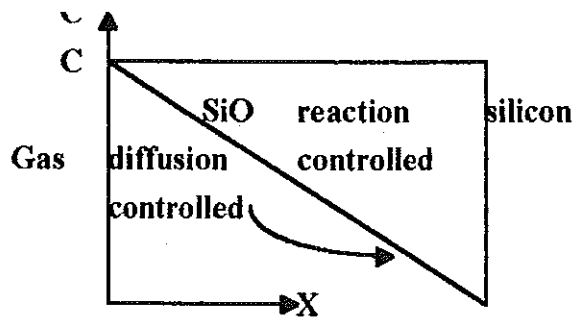


Fig. 3.6 Distribution of the oxidizing species in the oxide layer for the two limiting cases of oxidation. [After Grove(1965).]

Inspection of equation (3.20) reveals that when $D \gg K_s X_o$, $F = C_o K_s$ (reaction controlled); when $D \ll K_s X_o$, $F = DC_o / X_o$ (diffusion controlled) The limiting cases are illustrated schematically in Fig.3.6.

To arrive at a general initial condition of this equation, the total oxide thickness X_o is taken to consist of two parts: an initial layer of oxide X_i that might have been present on the silicon prior to the oxidation step under consideration. Thus the initial condition for this step is:

$$X_o = X_i \quad \text{at } t = 0 \quad (3.21)$$

The solution of the differential equation, Eq. (3.20), subject to the initial condition. Eq. (3.22), obtained by straightforward integration, is

$$X_o^2 + AX_o = Bt + AX_i + X_i^2 \quad (3.22)$$

which can be rewritten in the form

$$X_o^2 + AX_o = B(t + \tau) \quad (3.23)$$

where

$$A = \frac{2D}{K_S}(\text{cm}), B = \frac{2DC_o}{N}(\text{cm}^2/\text{s})$$

and

$$\tau = X_i^2/B + X_i/(B/A)$$

The quantity τ corresponds to a shift in the time co-ordinate which corrects for the presence of the initial oxide layer X_i . Solving for the oxide thickness as a function of oxidation time, we obtain.

$$X_o = \frac{A}{2} \left[\left(1 + \frac{t + \tau}{A^2/4B} \right)^{1/2} - 1 \right] \quad (3.24)$$

For short oxidation times, $t + \tau \ll A^2/4B$, we obtain the linear oxidation law,

$$X_o = \left(\frac{B}{A}\right)(t + \tau) \quad (3.25)$$

$$\frac{B}{A} = \frac{C_o K_g}{N} \quad (3.26)$$

B/A is referred to as the linear rate constant. For long oxidation times, $t \gg A^2/4B$, we obtain the parabolic oxidation law,

$$X^2 = Bt \quad (3.27)$$

It should be noted at this point, however that for most of the range the parabolic limit does not provide a good approximation. For this reason, simply dividing X^2 by t does not necessarily yield the true parabolic rate constant B , but rather it gives some quantity which may or not approximate B depending on the oxidation conditions and the time.

4. EXPERIMENTAL RESULTS AND DISCUSSION OF OXIDATION OF Si

4.1 Experiments

Prior to the oxidation, the samples were cleaned to eliminate both organic contamination arising from previous processing steps and handling. Such contamination, if not removed, can degrade the electrical characteristics of the SiO_2 formed as well as contribute to reliability problems. Particular matter was removed by ultrasonic scrubbing. The cleaning procedure is methanol (CH_3OH) for five minutes at 80°C , acetone (CH_3COCH_3) for five minutes at 80°C and dionized water for five minutes.

In the present method the thin SiO_2 films are fabricated in a controlled dry oxygen ambient in a computer controlled Rapid Thermal Annealer (RTA). The desired insertion and withdrawal rates, ramp (up and down) rates, gas flows are all programmable. Rapid Thermal Annealer is characterized by the advantage to carry out high temperature annealing in the range of some seconds up to few minutes. This is the basis for the manufacturing of very thin films and small structure used in submicron devices.

Si (100), n-type, $0.5\text{-}1\ \Omega\text{cm}$ with 10 mm by 10 mm dimension are introduced into a nitrogen filled quartz chamber. After switching a controlled oxygen flow of 1 l/min into the chamber, a step by step temperature time profile is executed as shown in Fig.4.1. Heating is provided by tungsten-halogen lamps. The SiO_2 growth occurs during higher temperature step with a duration between 30-180 s. A feedback system with an in situ pyrometer control the annealing temperature. Time is controlled by the microprocessor starting from a threshold temperature close to the set point.

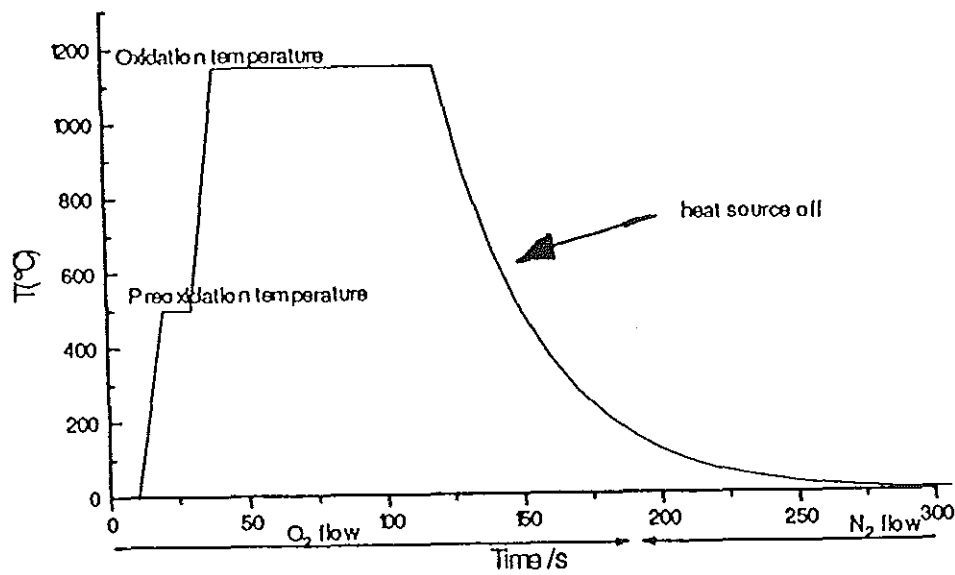


Fig. 4.1 Scheme of the whole thermal cycle of the RTA annealing.

The complete thermal cycle is described schematically in Fig. 5.1. All process were started with 10 s preheating period at 500 °C to get defined initial conditions in the chamber because of the memory effects due to slow cooling down of the quartz glass window from the previous process with different ramp rates. The samples were annealed for oxidation at temperatures of (100°C, 1050°C, 1100°C and 1150°C) and from 30 s - 180 s in step of 30's. 50 s after the heat source switching off the gas flow was changed from oxygen to nitrogen. Then, the samples were taken out and characterized.

4.2 Characterization

The characterization of SiO₂ on silicon substrates was done by using RBS, ellipsometr and transmission electron microscopy (TEM). The structural analysis and thickness measurement of the SiO₂ film formed was first characterized by RBS, and spectras are obtained. These obtained spectra were only random spectra. The thickness of SiO₂ was

determined by the shift of front edge of the Si signal with respect to its surface position by RUMP² simulation as shown in Fig. 4.2.

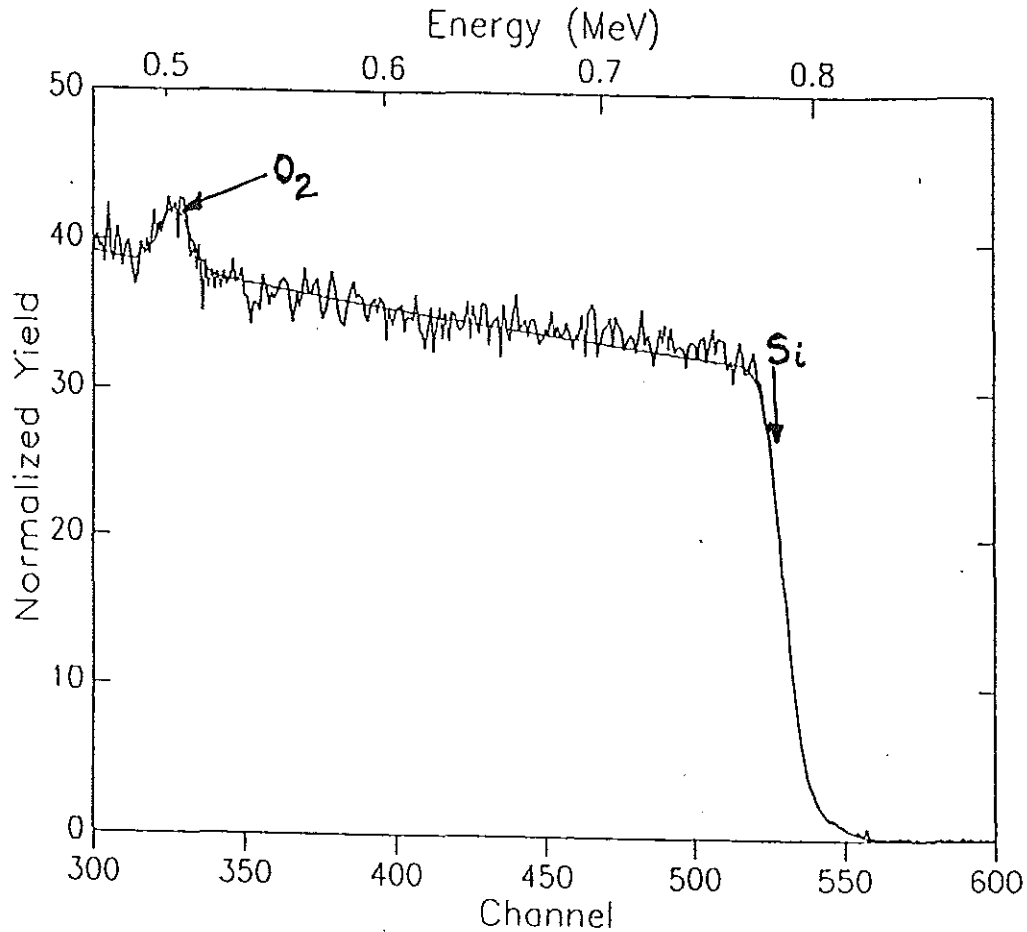


Fig.4.2 Rutherford backscattering spectra showing the formation of SiO₂ films and RUMP simulation during dry oxidation.

Fig.4.2 presents RBS spectra measured after oxidation. With increasing oxidation temperature and time the relative thickness of SiO₂ increases. The corresponding oxygen peak behaviors in situ measured show the higher temperature will produce higher SiO₂ thickness. The thickness of SiO₂ formed was also measured by spectroscopic phase modulate ellipsometer (SPME).

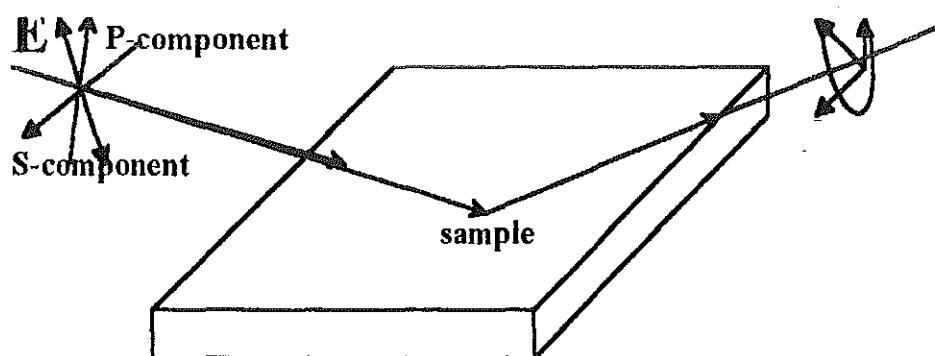


Fig. 4.3 Reflection of polarized light

The angle of incidence was near Brewster angle (70°). It is chosen because the SPME is more sensitive at this angle. The incident light was linearly polarized incident on the surface of sample at an angle of 70° and the reflected light is elliptically polarized as shown in Fig. 4.3.

Experimental measurements on films are taken at 1.5-4 eV energies in step of 0.5 eV. The experimental data were then compared with calculated $\tan\psi$ and $\cos\Delta$ spectra obtained from a single - layer abrupt interface model using reference spectra for substrate Si and SiO_2 .

4.3 Experimental Results and Discussion

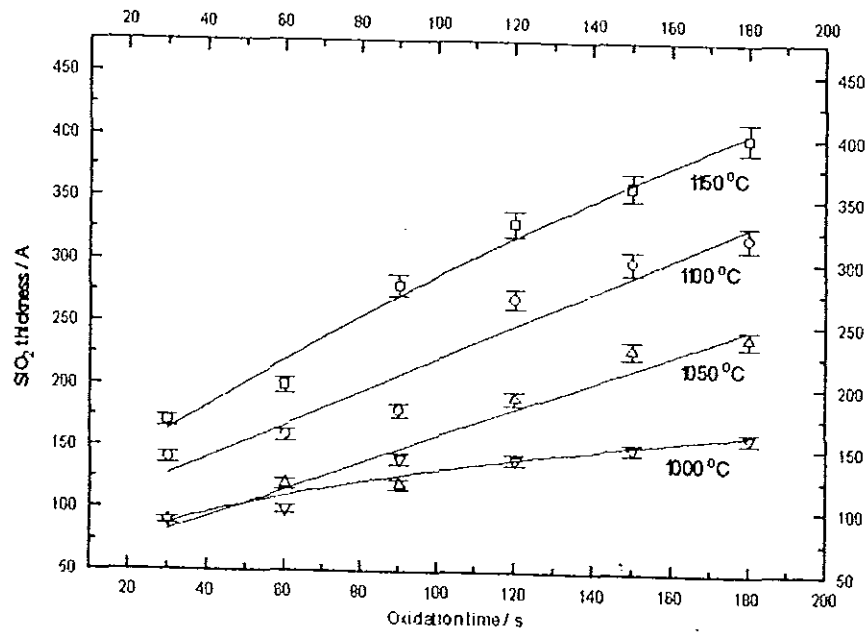


Fig. 4.4 (a) SiO_2 film thickness as a function of the oxidation time measured by RBS in dry oxygen ambient

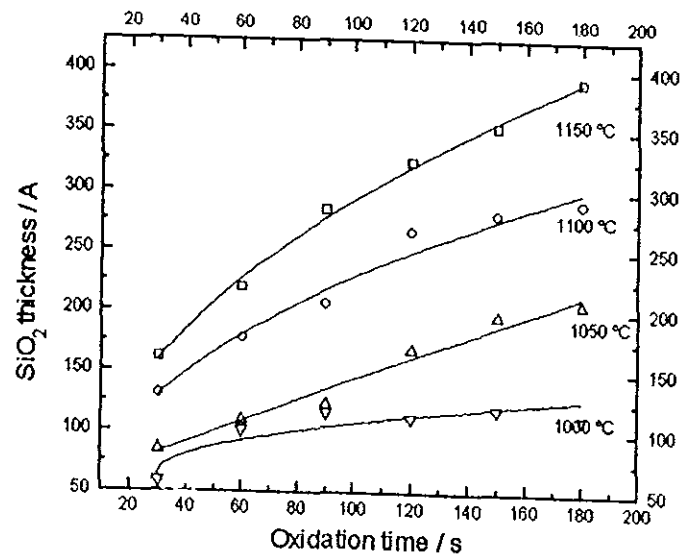


Fig. 4.4 (b) SiO_2 film thickness as a function of the oxidation time measured by ellipsometer in dry oxygen ambient.

The thickness of SiO_2 film versus oxidation time for different oxidation temperatures measured by Rutherford backscattering (RBS) and spectroscopic Phase modulate ellipsometr (SPME) is shown in Fig 4.4 (a) and (b) respectively.

Table II. Rate constant's for oxidation of silicon in dry oxygen ambient

$$[X^2 + AX_o = B(t + \tau)]$$

Oxidation				
temperature [$^{\circ}\text{C}$]	A[cm]	B[cm^2/s]	B/A[cm/s]	t[S]
1150	2.42×10^{-7}	8.15×10^{-14}	3.4×10^{-7}	3.4
1100	7.1×10^{-7}	4.08×10^{-14}	6.0×10^{-7}	11.3
1050	9.19×10^{-8}	1.06×10^{-14}	9.64×10^{-8}	46.0
1000	1.26×10^{-6}	2.9×10^{-15}	2.27×10^{-9}	169.4

The experimental data can be described with Deal and Grove oxidation kinetics formula with the linear rate constant (B/A), the parabolic rate constant B and the shift in time coordinate τ is given in table II. The values are comparable with those obtained by Deal and Grove [19]. Thermal oxidation of silicon was carried out in dry oxygen ambient at temperatures 1000-1150 $^{\circ}\text{C}$. The chemical reaction between the solid and gas occurs, leading to SiO_2 formation at the surface. There are two stages of oxidation. At time $t = 0$, oxidation occurs at the bare silicon surface or at a surface that only has a native SiO_2 on it. After a time $t > 0$, i.e., when an SiO_2 layer has formed on the silicon surface, one can envisage the oxidation to continue by one of the following two possible mechanisms: a) oxidant diffuses through the growing SiO_2 to the silicon- SiO_2 or b) silicon diffuses through SiO_2 -gas interface.

When the oxidant is the diffusing species, the reaction will occur at the SiO_2 -gas interface. The kinetics in either case will be determined by the availability of the diffusing species to the reaction interface and on the reaction at that interface. A large number of experiments have been carried out in the past to identify the diffusing species and to determine the kinetics. It was found that oxidation always occurs at silicon - SiO_2 interface and oxidant species diffuse to this interface. These two phenomena occur in series. Specifically, diffusion of the oxidant species to the Si - O_2 interface precedes the reaction at the interface except at oxidation time $t = 0$. At any time greater than zero, the slower of the two phenomena will control the kinetics. In simple terms, at $t = 0$ the reaction at the Si - gas interface control the kinetics. As the SiO_2 thickness increases, the diffusion through the SiO_2 starts playing a role in determining the kinetics, since diffusion is found to be the slower process. At sufficiently large SiO_2 thickness (approximately a few hundred angstroms), the diffusion through SiO_2 controls the kinetics completely.

Comparison of the two thickness measuring methods was done. It was found that RBS measurement results are comparably good with ellipsometric measurement results. In Fig. 4.5 the comparison of the two measuring methods is presented. This tells about the reliability of RBS SiO_2 film thickness measurement.

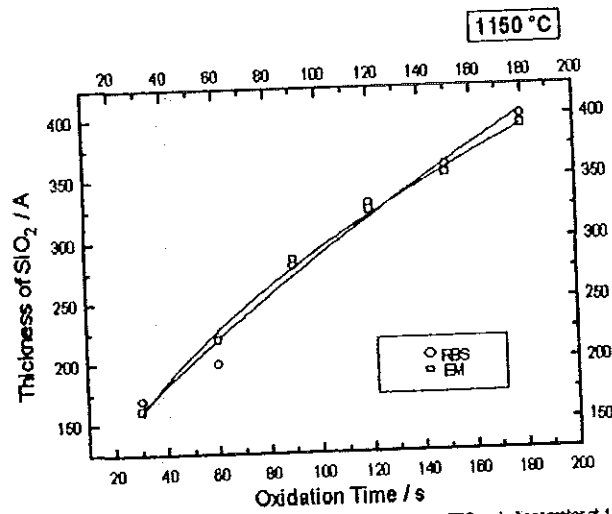


Fig. 4.5 Comparison of SiO₂ thickness as a function of oxidation time for RBS and ellipsometer at 1150°C

The microstructure of SiO₂ in (100) Si is shown in the cross-sectional transmission electron microscopy (X-TEM) for $T = 1150^{\circ}\text{C}$ and 180 s in Fig. 4.6. The SiO₂ layer shows excellent uniformity and sharp interface.

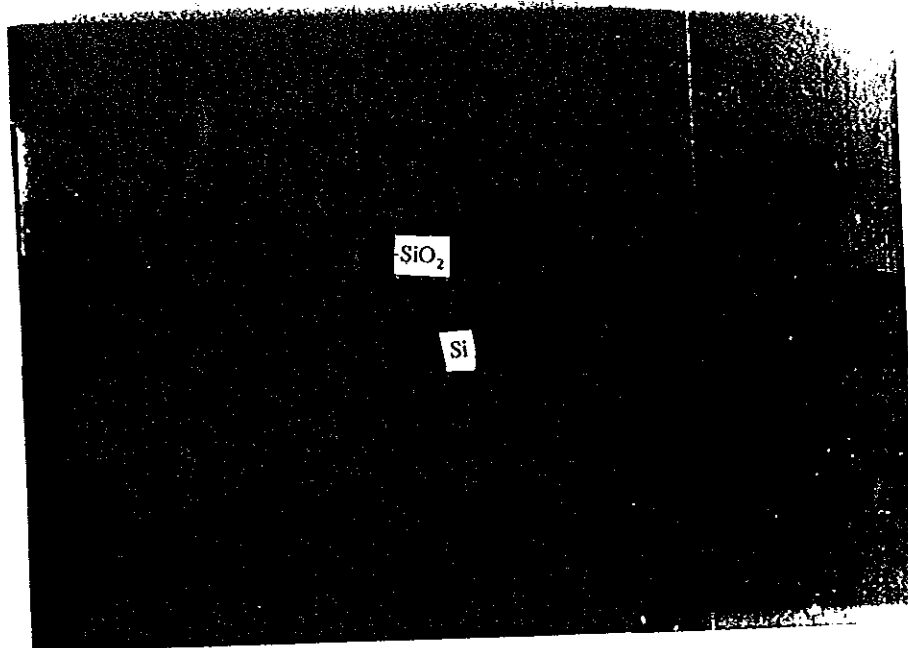


Fig. 4.6 X-TEM micrograph of SiO₂ in (100) Si for 1150°C at 180 s.

5. EXPERIMENTS, RESULTS AND DISCUSSION OF OXIDATION OF SURFACE CoSi_2

5.1 Experiments

Surface CoSi_2 on Si (100) substrate with thickness 1440 Å, resistivity $13 \mu\Omega\text{cm}$ and $\chi_{\text{min}}=9.7\%$ was used as a sample to study the oxidation kinetics and its stability after oxidation. Prior to oxidation the resistivity measurement was performed by the method of Van der Pauw.

The same cleaning procedure was used as in the case of Si (section 4.1). The thermal oxidation was carried out between 1000°C and 1150°C using the Rapid Thermal Annealer (RTA) in dry oxygen ambient and constant flow rate of 1 l/min. The temperature program was also the same in the case of Si as shown in Fig.4.1 and as described in section (4.1).

After oxidation the samples were characterized by resistivity measurement, to monitor the structural stability, crystal quality and thickness of SiO_2 formed, use was made RBS 1.4 MeV He^+ ions and X - TEM.

The RBS spectra both for random and aligned spectra were taken and the thickness measurement and χ_{min} evaluation were done using the RUMP program. The thickness of the formed SiO_2 film was determined by measuring of the width of the oxygen signal, the width of the step due to silicon in the SiO_2 layer, and by determining the shift of the front edge of the Si signal with respect to its surface position. These values were internally consistent and an average value was used. The results of a channeled spectrum and a random spectrum can be used to accurately determine χ_{min} for the measuring the of crystal

quality. This can be performed using the DIVIDE command in Rump Program. The RAW mode of the counts should always be used. A channeled spectrum divided by a random spectrum gives us χ_{can} . The morphology of the sample was analyzed by cross-section transmission electron microscopy (X-TEM).

5.2 Results and Discussion

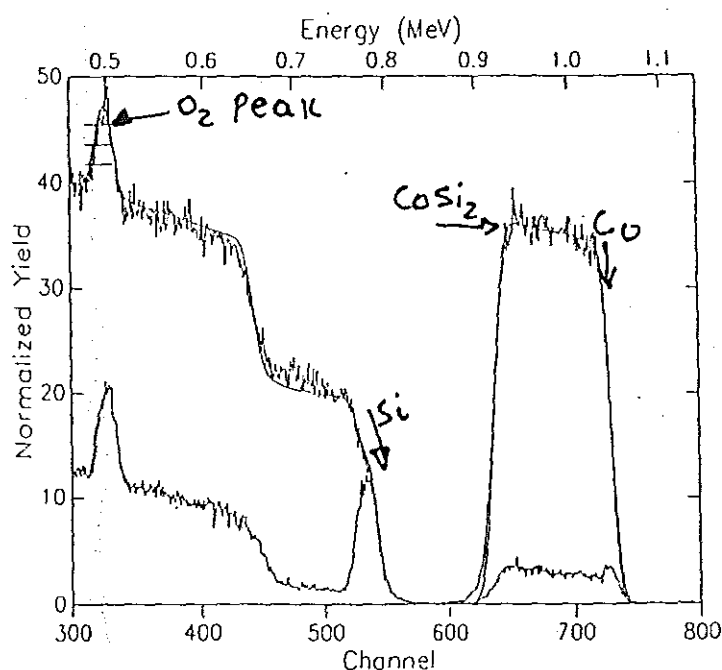


Fig.5.1 The random and aligned RBS spectra for oxidation of surface CoSi_2 .

Figure 5.1 shows the random and the aligned RBS spectra for oxidation of surface CoSi_2 over silicon substrate after oxidation dry oxygen ambient. The RBS spectrum of oxidation of surface CoSi_2 shows oxygen(O_2) peak and CoSi_2 peak. The peaks occur around 300- 325 channel numbers and 700-800 channel numbers respectively. It has been found, that CoSi_2 film phase, as well as the CoSi_2 thickness, remain unchanged as the oxidation proceeds.

The solid line in Fig. 5.1 represents an RBS simulation of the random spectrum, produced by the RUMP Program. From this simulation, measurement of the width of the oxygen signal and measurement of the width of step due to the silicon in the SiO_2 layer that the thickness of the SiO_2 layer formed was determined by taking the average of these three values.

The crystallinity measured by the minimum channeling yield $\chi_{\min}$ improved with increasing oxidation temperature up to 1150 °C for which a $\chi_{\min}$ of 3.7 % of surface CoSi_2 after oxidation was obtained. The resistivity before and after oxidation was determined using the Van der Pauw method (section 2.3). The results of this resistivity measurement before oxidation was between (0.196 - 0.281 $\mu\Omega\text{cm}$) and after oxidation between (0.120 - 0.192 $\mu\Omega\text{cm}$). These results of measurement indicates the resistivity decreases after oxidation and this is one of the desired properties for an interconnect material.

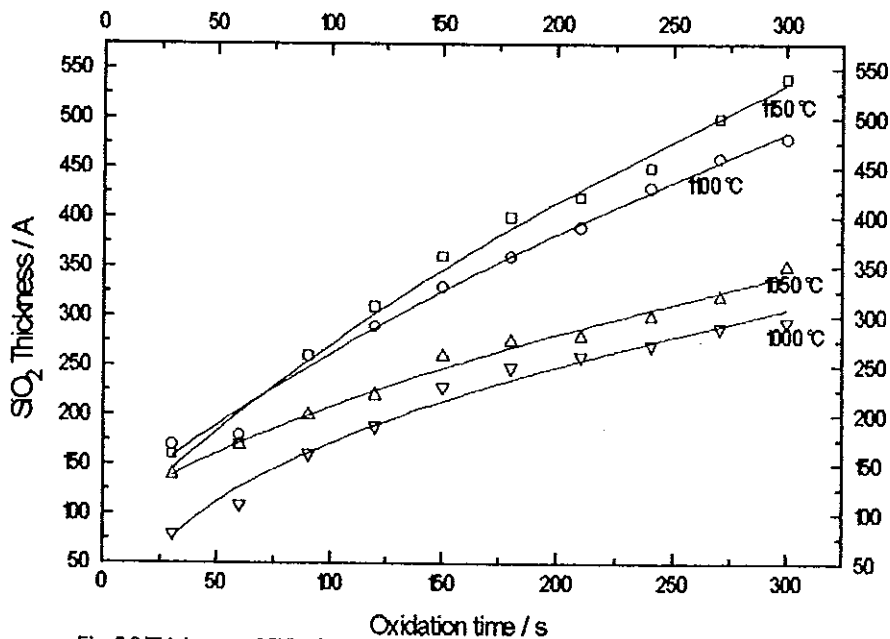


Fig. 5.2 Thickness of SiO_2 formed versus oxidation time for different oxidation temperatures .

Figure 5.2 shows the thickness of SiO_2 formed measured using RBS versus the oxidation time. An oxidation model for the surface CoSi_2 is the Deal-Grove [19] oxidation model. The analysis of experimental data was carried out using this oxidation model, that is the experimental results of thickness dependence of SiO_2 formed versus oxidation time was obtained by using the linear-parabolic relationship. The experimental results of SiO_2 formed versus oxidation time for different oxidation temperatures and different oxidation times is shown in Fig. 5.2. It can be noted that the fit of the model to the experimental results is good. As can be observed in Fig. 5.2. The thickness of the SiO_2 layer increased with increasing oxidation temperature or/and oxidation time.

The oxidation rate constants B/A and B , which are obtained from the curve fitting by origin - 2 computer software program are summarized in table III.

Table III
Rate of Constants for Oxidation of Surface CoSi_2
in Dry Oxygen Ambient

<u>Temperature</u> [°C]	<u>A[cm]</u>	<u>B[cm/s²]</u>	<u>B/A[cm/s]</u>	<u>t[s]</u>
1150	62.4×10^{-6}	1.88×10^{-13}	3.0×10^{-8}	29.3
1100	5.91×10^{-6}	1.495×10^{-13}	2.5×10^{-8}	49.7
1050	5.90×10^{-7}	4.04×10^{-14}	6.8×10^{-8}	38.4
1000	2.6×10^{-7}	3.06×10^{-14}	1.18×10^{-7}	18.1

From this table and also from Fig.5.2; it can be inferred that the curves are more linear for temperatures 1000 and 1050 °C than 1100 and 1150 °C. Because of the higher sensitivity of the linear rate constant to time of oxidation and temperature of oxidation i.e. for short time of oxidation and lower temperature we have more of linear rate of constant. The sensitivity of linear rate of oxidation becomes more serious at the transition time from linear to parabolic growth decreases to relatively very small value. The rate is lower for lower temperatures (1000 and 1050 °C) this is may be one of the reasons why we observe the gap in Fig.5.2. Using eq.(3.2); The activation energy for surface CoSi_2 is estimated to be 1.8 eV. It was found by other authors to be $(1.3 \pm 0.3 \text{ eV})$ for dry oxidation of surface CoSi_2 . It should be pointed out that, because of higher sensitivity of the linear rate at short time of oxidation constant the estimated activation energy for parabolic rate of constant is less accurate.

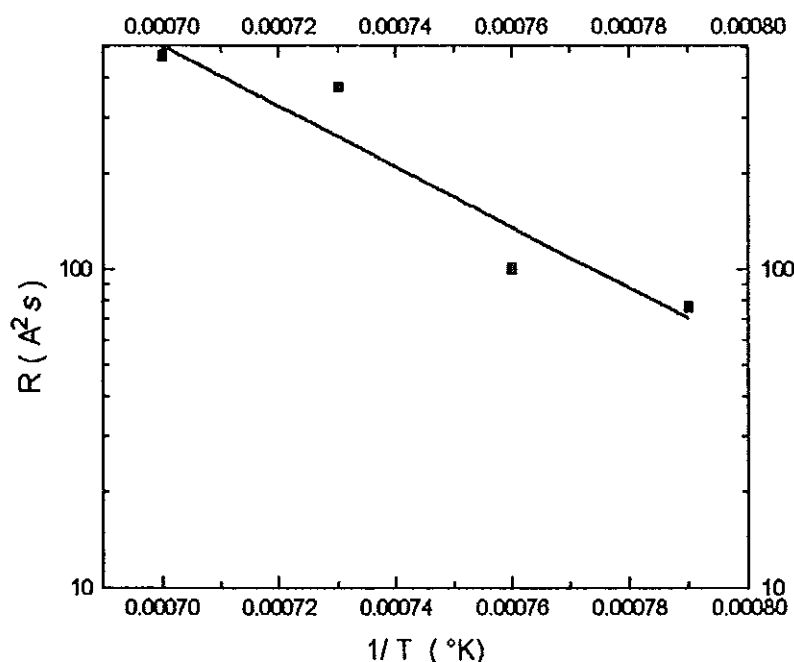
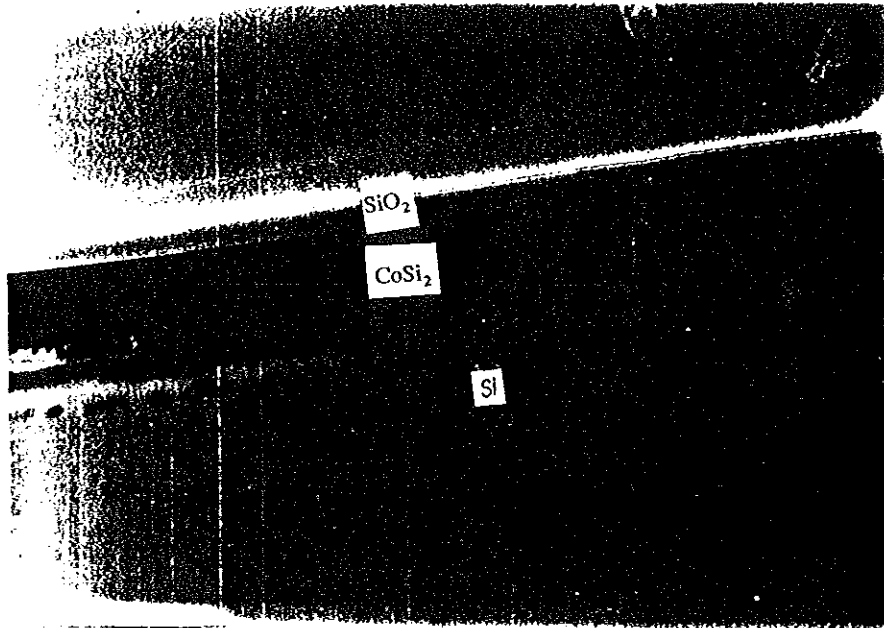


Fig. 5.3 Arrhenius plot of SiO_2 growth rate on surface CoSi_2 for dry oxygen ambient oxidation.

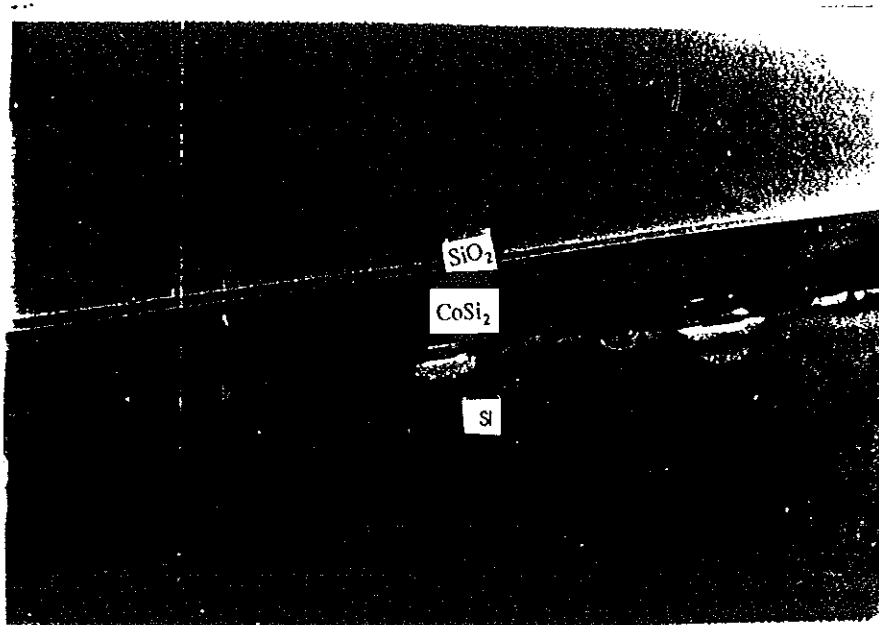
The microstructure of SiO_2 is shown in fig.5.4 from the cross-sectional transmission electron microscopy (X-TEM) for temperatures 1150 °C and 1100 °C at 300 s. The SiO_2

layer shows excellent uniformity and sharp interface with CoSi_2 for both 1100 and 1150°.

The CoSi_2 layer after oxidation is uniform and stable; its interface with Si is also sharp for 1100°C. But it shows non-uniformity and instability at the interface with silicon for 1150°C oxidation.



1000 °C at 300 s.



1150 °C at 300 sec.

Fig.5.4 X-TEM micrograph of SiO_2 on surface CoSi_2 for 1100 and 1150 °C
at 300sec.

6. OXIDATION OF BURIED CoSi_2 (Si / CoSi_2 / Si)

6.1 Experiments

Buried CoSi_2 on Si(100) substrate with 1960 Å Si cap, 1455 Å CoSi_2 film, with resistivity $13 \mu\Omega\text{cm}$ and χ_{Si} for CoSi_2 9.7% was used as a sample to study the oxidation Kinetics and its interface stability after oxidation. Prior to oxidation the resistivity measurement was performed by the method of van der pauw. The same cleaning procedure was used as that of Si and surface CoSi_2 . The temperature program was as shown in Fig. 4.1 and as described in section 4.1.

The samples were analyzed by Van der pauw, RBS and ion channeling to measure the thickness of SiO_2 formed and the degree of crystallinity. A 1.4 MeV He^+ with backscattering angle of 170° was used. The RBS Spectra were evaluated by RUMP program. The interface and micro structure of the samples were analyzed by cross-sectional transmission electron microscopy (X-TEM).

6.2 Results and Discussion

Rutherford backscattering (RBS) and Ion channeling spectra are shown in Fig. 6.1 for oxidation of buried CoSi_2 (Si/ CoSi_2 /Si). The RBS spectrum shows the Si top layer, buried CoSi_2 layer keep intact after oxidation no change in stoichiometry. The single-crystal structure of CoSi_2 confirmed by the channeling spectrum, with χ_{Si} = 4.7-5.6%. The solid lines shown a RUMP program simulation. The thickness of SiO_2 layer formed was evaluated by taking the average of the three measurement results as mentioned and described in section 5.2.

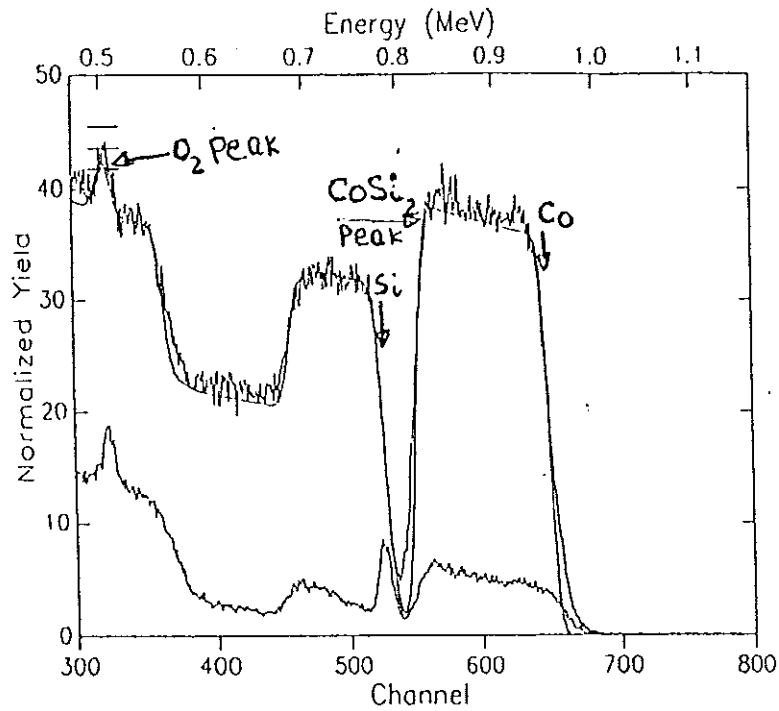


Fig. 6.1 Random and Channeling Spectra for Buried CoSi_2 at 1150°C

The resistivity decreases from ($28.8\text{-}27.6\ \mu\Omega\text{cm}$) to $13.3 - 12.3\ \mu\Omega\text{cm}$). This shows buried CoSi_2 electrical property improves after oxidation at higher temperatures such as 1150°C . It is one of the most desired properties of inter connecting materials (1,2,4,6,8).

The oxidation model used to fit the experimental data was Deal and Grove [19]. As can be seen the linear-parabolic law fits to the experimental data very well as shown in Fig.6.2.

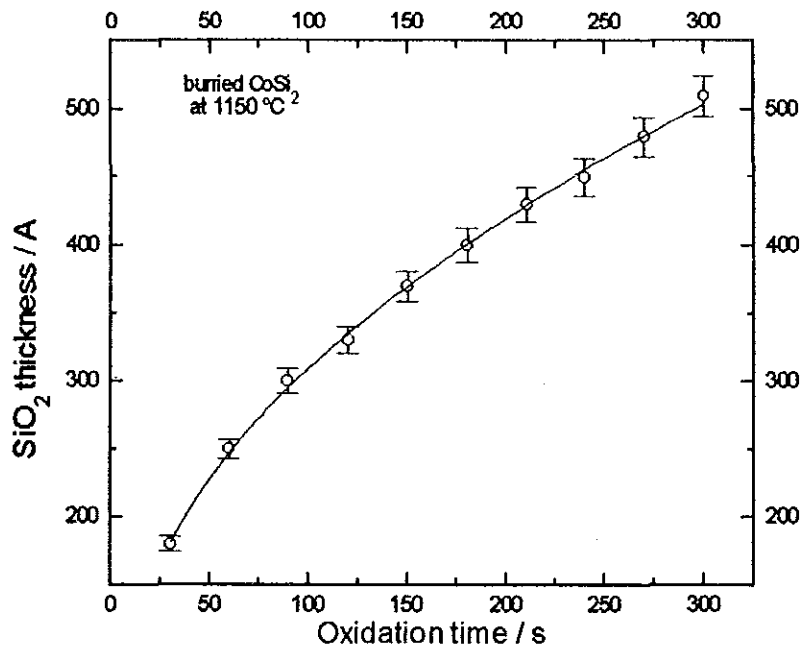


Fig. 6.2 thickness versus oxidation time for buried CoSi_2

The microstructural investigation was carried out by X-TEM. The interface between SiO_2 -Si is not sharp, between Si- CoSi_2 is also not sharp and between CoSi_2 -Si-substrate is sharp and we observe grooves. This is may be due to the shortage of oxygen and this strained interface is formed.

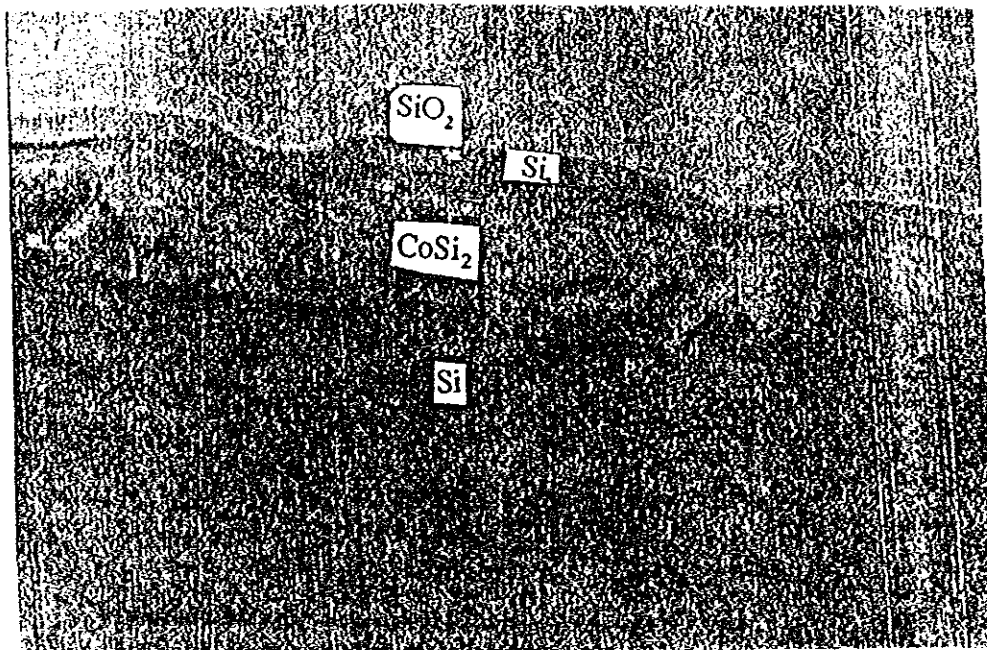
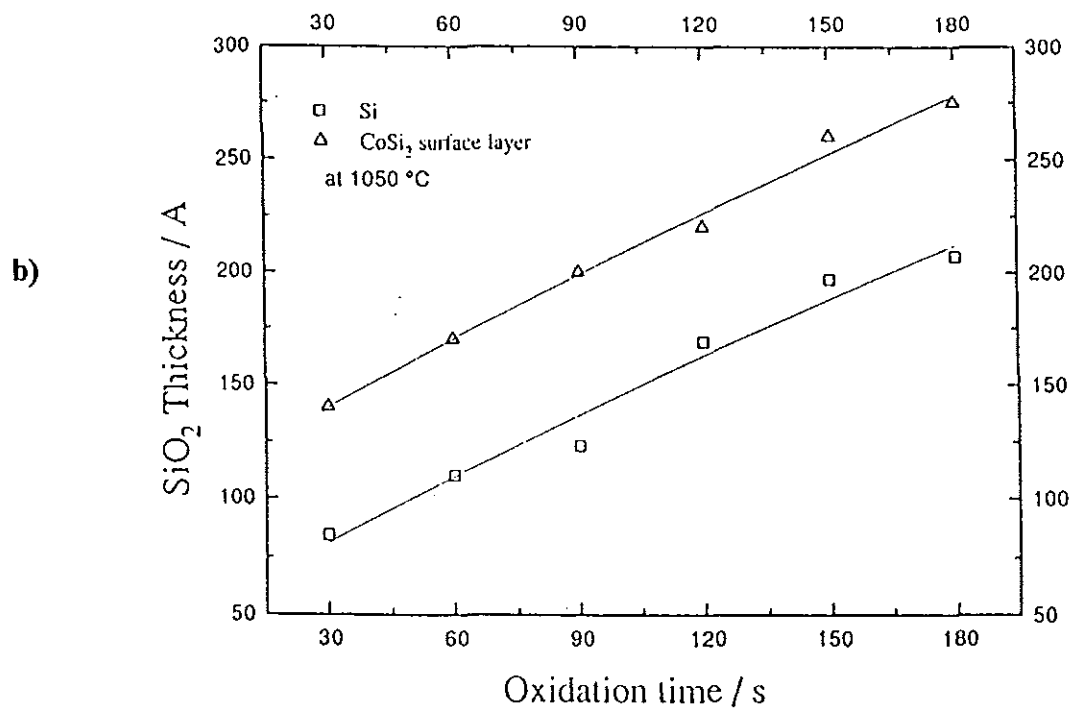
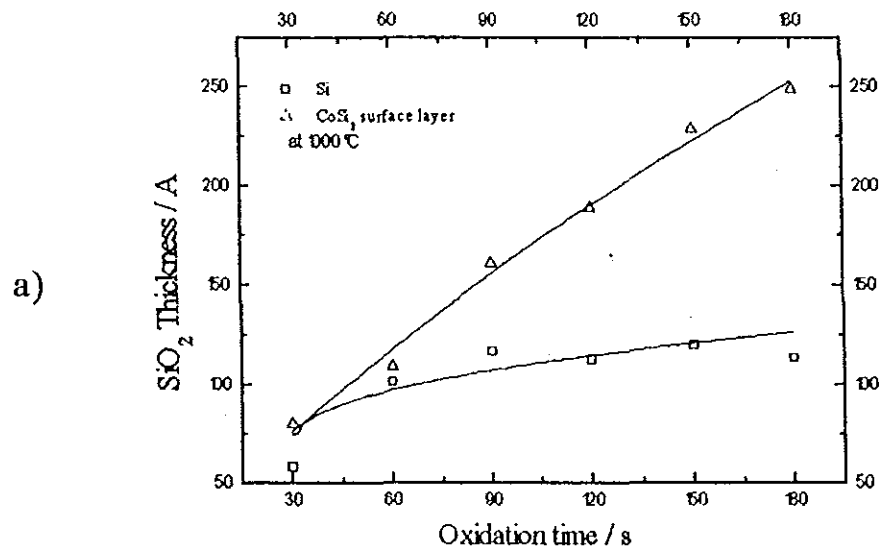


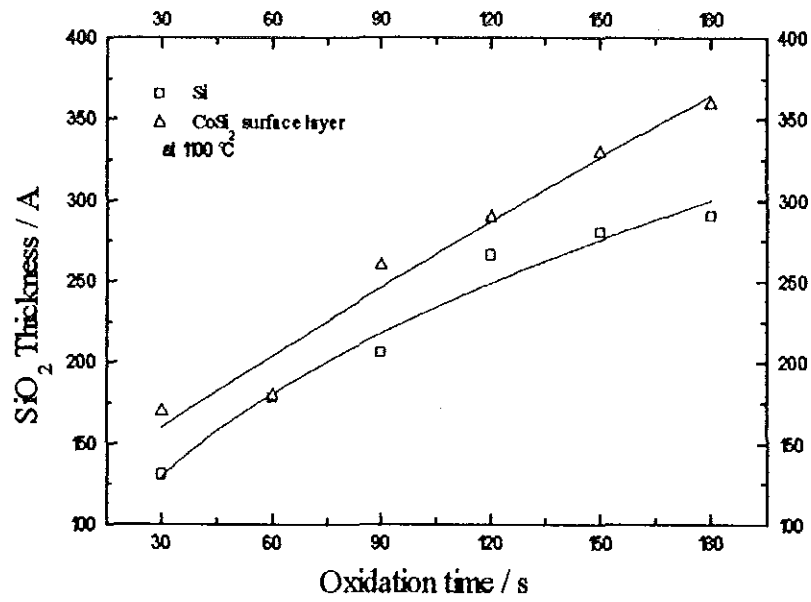
Fig. 6.3 X-TEM Micrograph of Buried CoSi_2 Capped with Si layer at 1150°C and 300 s.

7. COMPARISON OF OXIDATION OF Si, SURFACE CoSi_2 AND BURIED CoSi_2

The comparison of oxidation of Si and surface CoSi_2 is made for different temperatures (1000, 1050, 1100 and 1150°C) as shown in Fig. 7.1 (a), (b), (c), (d) respectively.



c)



d)

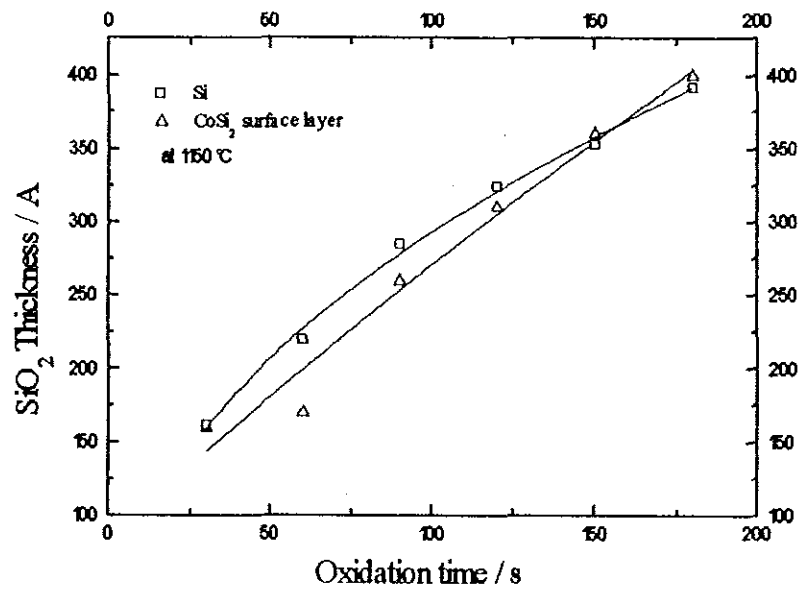


Fig. 7.1 Comparison of oxidation rate of Si and surface CoSi₂ for different temperatures.

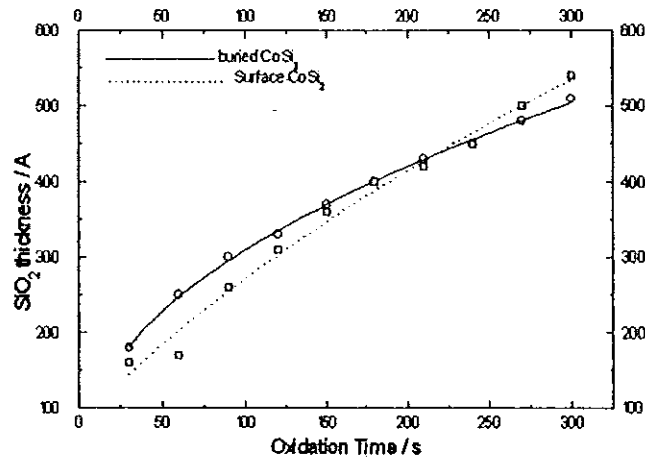


Fig.7.2. Comparison of oxidation rate of buried and surface CoSi₂

The oxidation rate of surface CoSi₂ is higher than the oxidation rate of silicon temperatures (1000, 1050, 1100 °C) for the same length of oxidation time. This due to the linear rate constant i.e, the linear rate constant for CoSi₂ is larger than that of silicon oxidation at a given temperature [12]. This linear rate constant is dominant at short time of oxidation. That is why the rate at these temperatures is higher for CoSi₂. But this is not true as we can see from Fig. 7.1. (d) the comparison of oxidation of surface CoSi₂ and silicon for 1150 °C. The silicon oxidation rate is higher may be because of faster transition at this temperature from linear rate to parabolic rate. Since linear rate is more sensitive at the transition time from linear to parabolic growth it decreases relatively to a small value.

The oxidation rate of buried and surface CoSi₂ is shown in fig. 7.2. from the figure we can see that rate is higher for buried than for surface CoSi₂ for 1150°C in a similar way to the rate of silicon and surface CoSi₂ for 1150°C. That is, the rate is the same for Si and buried CoSi₂.

8. CONCLUSION

Rapid thermal annealer (RTA) in dry oxygen ambient is a good and reliable method of producing thin SiO_2 layers for a short time of oxidation. The oxidation kinetics of Si that is thickness of SiO_2 formed layer versus oxidation time obey a linear parabolic law (Deal and Grove Model). The interface between SiO_2 -Si is sharp and SiO_2 -Si is sharp and SiO_2 layer shows excellent uniformity.

Single crystalline surface CoSi_2 is found to show a good crystal quality up to ($\chi_{\text{am}}=3.7\%$) in dry oxygen ambient at 1150°C and 1100°C . The interface between Si- CoSi_2 is sharp at 1100°C but the interface between SiO_2 - CoSi_2 shows grooves but still the CoSi_2 layer is not destroyed at this higher temperature. The resistivity of surface CoSi_2 decreases after oxidation. Single crystalline buried CoSi_2 is also found to show good crystal quality (4.7%) after oxidation at 1150°C and the interface between SiO_2 -Si cap and Si cap- CoSi_2 is not sharp but the layers show uniformity. Both surface and buried CoSi_2 the oxidation model (Deal - Grove) is found to be a good model. The resistivity of buried CoSi_2 decreases after oxidation in dry oxygen ambient.

The oxidation rate of surface CoSi_2 is higher than that of Si for (1100°C , 1050°C , 1000°C) and the oxidation rate of Si is higher than that of surface CoSi_2 for 1150°C . The oxidation rate of buried CoSi_2 and Silicon are the same. The activation energy of surface CoSi_2 is found to be 1.8 eV.

Both surface and buried CoSi_2 are the possible potential materials that can be used in VLSI technology. It is possible to produce an oxide layer with thickness $\leq 100 \text{ \AA}$.

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