CHAPTER THREE : EXPERIMENTAL TECHNIQUES

3.0 Introduction

In this work, the silicon wafers were subjected to two separate treatments . The first set of wafers were contaminated with solutions containing different metals. The second set were oxidized in a furnace at different temperatures and durations. After the treatment, the UV-irradiation effect of the effective lifetime were measured using laser-microwave photo-conductive decay (LM-PCD) technique.

3.1 Metal Contamination

A set of wafers was dipped into the deionised water containing metals. Five different types of metal were used and their concentrations are listed in the Table 3.1. These metals are iron (Fe), copper (Cu), nickel (Ni), zinc (Zn) and aluminium (Al), with concentrations prepared in accordance once with the USA atomic spectroscopy standard of 1000 ppm Fe (7439-89-6), Cu (7440-50-8), Ni (7440-02-0), Zn (7440-66-6) and Al (7429-90-5) in 2 % of nitric acid (HNO_3) (7697-37-2) as a solution matrix. This solution was then diluted in the deionised water guided by the equation (3.1) below

$$m_1 V_1 = m_2 V_2 \tag{3.1}$$

where m_1 and m_2 are the metal concentrations and V_1 and V_2 are the volumes respectively.

Contaminants	Concentration in deionised water / ppb
Iron (Fe)	0.1 , 0.6 , 1.0
Copper (Cu)	0.5 , 5.0 , 10.0
Nickel (Ni)	0.5 , 2.0
Zinc (Zn)	0.1 , 0.5 , 1.0
Aluminium (Al)	0.5 , 1.0 , 10.0

Table 3.1 : Metal contaminant concentrations in deionised water introduced to the sample.

Steps for the preparation of surface contaminated wafer is shown in Figure 3.2. The atomic spectroscopy standard was diluted in the 100 mℓ volumetric flask first before being spike into the 15000 mℓ quartz tank. The spiking volume into the quartz tank was calculated based on equation (3.1) :

$$V_{p2} = \frac{1.5m_c}{V_{p1}} \tag{3.2}$$

where V_{p1} and V_{p2} are the spiking volumes of the flask and the quartz tank respectively in milliliter (mℓ). The unit for the desired metal concentration, m_c is parts per billion (ppb). The contaminated deionised water was stirred with a quartz rod to make sure the metal contaminant was evenly distributed in the water.

After the solution has stagnated, the clean wafer was dipped in the solution for about 180 s. The wafers were then dried in the IPA (Isopropanol Alcohol) for 90 seconds. These surface-contaminated wafers were stored in the P.P (Polypropylene)

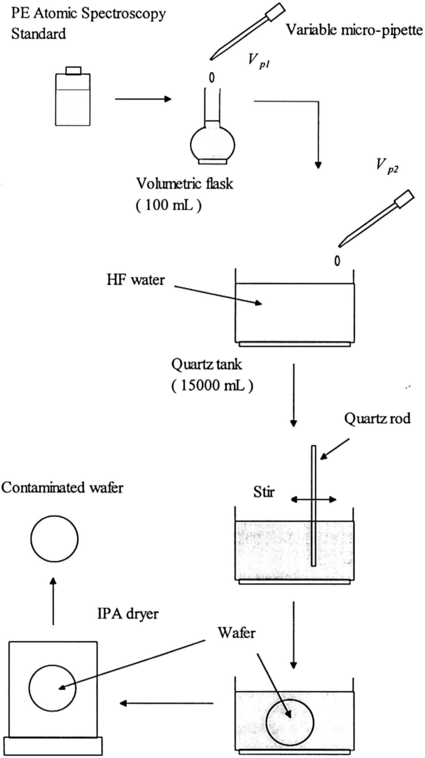

Figure 3.2 : Experimental steps for metal contamination of Si wafer (SZ)

box and sealed in the polyethylene bag to avoid possible contamination from the surroundings during transferred to another laboratory before metal concentration and effective lifetime measurements.

3.2 Thermal Oxidation

A second set of wafers were oxidized in a horizontal furnace (Model 2610, SVG Systems Ltd., U.K) at different temperatures and oxidation durations. The following sections will describe the resistance-heated oxidation furnace system, its temperature profile and thermal cycle for a wafer oxidation process.

3.2.1 The Furnace

The basic setup of the thermal oxidation furnace is shown in Figure 3.3. The furnace consists of resistive filaments and a cylindrical fused-quartz tube in which the silicon wafer is held vertically in a slotted quartz boat in three possible heating zones. These corresponding internal heating zones are known as load (LZ), center (CZ) and the source zones. The LZ is about 80 cm from end cap. The separation between the adjacent zones is about 13 cm. The furnace can be operated in either purified dry oxygen, nitrogen or water wafer is held vertically in a slotted quartz boat in three possible heating zones. These corresponding internal heating zones are known as load (LZ), center (CZ) and the source zones. The LZ is about 80 cm from end cap. The separation between the adjacent zones is about 13 cm. The furnace can be operated in either purified dry oxygen, nitrogen or water vapor. These three different heating zones can be individually controlled and three thermocouples external to the furnace tube are used to measure their temperatures (T_{CS}, T_{CC} and T_{CL}). The temperatures were monitored by preparation using Yokogawa LR8100 temperature plotter. Their reading directly reflect the internal temperature profile of the furnace.

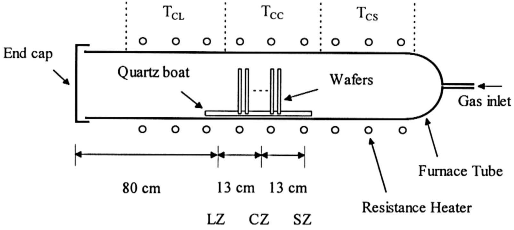

Figure 3.3 : Schematic cross section of the resistance-heated oxidation furnace

3.2.2 Temperature Profile of the Furnace

Before the furnace is used for the wafer oxidation, the axial temperature profiles of the LZ, CZ and SZ are maintained to be fairly flat with respect to each other. The furnace settings as given below :

(i) Air pressure : 105 psi

(ii) Oxygen pressure : 27 psi

(iv) Cooling water temperature : 31 °C

(iii) Cooling water flow rate : 1.5 liter/min

(v) Oxygen flow rate : 0.35 liter/min

(vi) Room temperature : 25 °C

The flat axial temperature profile is important since any significant thermal gradient will cause non-uniform oxidation in the wafer surfaces. Hence, a relatively flat (±1.5°C) axial temperature across the three zones in the tube are needed.

The 2^k factorial design[89] was initially used to determine the spill-over effects of different heating rates in the three zones. Using the three setting temperatures as independent factors with the high (H) and low (L) values at ±30 °C from the set temperature, T_O . Eight treatment combinations were required for this 2^3 factorial design. The response for a T_O of 600 °C is shown in the form of measured temperatures (Table 3.2) and deviation from T_O for each zone (Table 3.3). T_{cs}, T_{cc}, T_{cL} are thermal controller setting temperatures and T_{os}, T_{oc}, T_{oL} are measured temperatures at SZ, CZ and LZ respectively.

Treatment Combination			Temperature Recorded / °C					
T_{CS}	T_{CC}	T_{CL}	T_{OL}		T_{OC}		T_{OS}	
L	L	L	599.8	599.7	594.0	593.6	581.1	580.9
H	L	L	603.4	603.5	605.2	605.4	606.6	606.3
L	H	L	644.3	645.6	637.5	637.5	613.1	611.8
H	H	L	647.0	648.4	647.0	647.6	636.8	637.2
L	L	H	611.9	612.0	599.7	599.3	582.5	581.7
H	L	H	615.3	615.0	610.3	610.0	609.0	608.6
L	H	H	655.8	656.0	643.4	643.6	615.3	614.3
H	H	H	658.1	659.4	652.3	652.3	639.4	638.2

Table 3.2 : Two sets of measured temperature in LZ (T_{oL}), CZ (T_{oc}) and SZ (T_{os}).

The estimated effects for three main factors and their interaction effects using 2^k factorial design were analyzed by StatGraphics Plus (Statistical Graphics Corporation,

Treatment Combination			Deviation, (T - 600) / °C		
T_{CS}	T_{CC}	T_{CL}	T_{OL} - 600	T_{OC} - 600	T_{OS} - 600
L	L	L	-0.3	-6.2	-19.0
H	L	L	3.5	5.3	6.5
L	H	L	45.0	37.5	12.5
H	H	L	47.7	47.3	37.0
L	L	H	12.0	-0.5	-17.9
H	L	H	15.2	10.2	8.8
L	H	H	55.9	43.5	14.8
H	H	H	58.8	52.3	38.8

Table 3.3 : Average deviation of three zones from the set temperature (T_O).

USA). Their results are summarized in Table 3.4. Since the effect of T_{CC} controller setting temperature is largest compare to others, a small variation of it will produce a significant different on three temperatures recorded in the experiment. The interaction effects appear to be small relative to the three main effects. It does not appear to have as large an impact on the temperature deviation as the main effects. The largest interaction effect among them is T_{CS}-T_{CC} .

Main effect / °C	LZ	CZ	SZ
T_{CS}	3.13	10.19	25.18
T_{CC}	44.25	42.96	31.18
T_{CL}	11.48	5.39	1.90

Interaction / °C	LZ	CZ	SZ
T_{CS} - T_{CC}	-0.33	-0.89	-0.90
T_{CS} - T_{CL}	-0.10	-0.46	0.18
T_{CC} - T_{CL}	-0.48	0.11	0.18
T_{CS} - T_{CC} - T_{CL}	0.15	-0.04	-0.45

Table 3.4 : Average main and interactions effects of controller setting temperature.

Treatment combination of HLL (T_{cs} = 630 °C, T_{cc} = 570 °C and T_{cL} = 570 °C) in Table 3.3 gives the best thermal controller setting values for the lowest deviation values. To minimize the deviations further, a similar experiment is needed by using the treatment combination with lowest deviation values and two high and low levels in each factor.

The 2^k factorial design is tedious and time consuming for optimizing the temperature settings. It was noticed that there exist a relationship between the set temperature, T_O for a profile and the difference between the setting temperature(T_{cL} , T_{cc} and T_{cs}) and the measure temperature (T_{oL}, T_{oc} and T_{os})(Figure 3.4). A set of empirical equations to determine the thermal controller setting values was extracted using the trend observed in Figure 3.4. These are written down in Equation (3.3) below

For load zone,
$$T_{cL} = T_o + \Delta T_{oL} \quad °C$$
$$\Delta T_{oL} = 0.1050\ T_o - 91.5556$$

For center zone,
$$T_{cc} = T_o + \Delta T_{oc} \quad °C$$
$$\Delta T_{oc} = 0.0420\ T_o - 63.0000$$

For source zone,
$$T_{cs} = T_o + \Delta T_{os} \quad °C$$
$$\Delta T_{os} = 0.0020\ T_o + 15.4000 \tag{3.3}$$

where T_O is the set oxidation temperature. The deviations from set oxidation temperature were not more than ±1.5 °C as shown in Figure 3.5. To use Table 3.5, for example, if the required profile is to be at 900 °C, the setting values on the controller should be $T_{cL} = 903$ °C, $T_{cc} = 875$ °C and $T_{cs} = 917$ °C.

Target Oxidation Temperature, T_O / °C	ΔT / °C		
	$T_{CL} - T_O$	$T_{CC} - T_O$	$T_{CS} - T_O$
600	-29	-38	17
650	-23	-36	17
700	-16	-34	17
750	-13	-32	17
800	-8	-29	17
850	-2	-27	17
900	3	-25	17
950	8	-23	17
1000	13	-21	17

Table 3.5 : ΔT values for set oxidation temperatures from 600 °C to 1000 °C

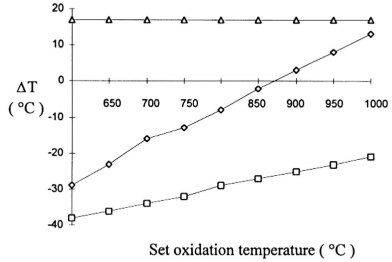

Figure 3.4 : A graph of ΔT against set oxidation temperature

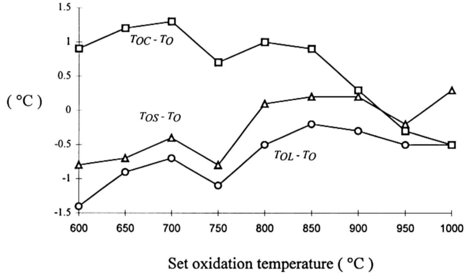

Figure 3.5 : Deviation values for SZ, CZ and LZ

3.2.3 Thermal Cycle for Oxidation

The wafers were put in the middle of the quartz boat with the two dummy wafers in front of the first wafer and after the last wafer. The wafers were preheated on the entrance before the quartz boat was pushed into the quartz tube. After the oxidation time needed by the experiments was fixed as shown in Table 3.6, the quartz boat was pulled out from the quartz tube. The following were the push/pull rate and time needed by the thermal oxidation process (Figure 3.6).

The thermal oxidation process was completed after the quartz boat was pulled out from the quartz tube. The wafers were allowed to cool down to room temperature before being stored in the polypropylene box (P.P box).

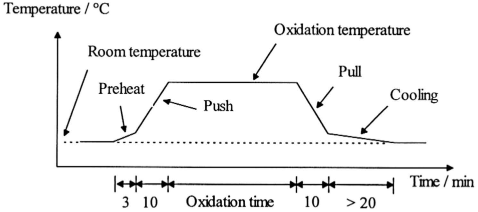

Figure 3.6 : The ramping time for the wafer in the furnace.

Oxidation Temperature / °C	Oxidation Time / min
700	10 , 20 , 40 , 80 , 160 , 300
900	10 , 20 , 40 , 80 , 160 , 300
1000	10 , 20 , 40 , 80 , 160 , 300

Table 3.6 : Oxidation temperature and time for experiments

3.3 Measurement Techniques

After the wafers were contaminated with different metals or thermally oxidized, the contaminant levels on the surface or the oxide thickness were measured. For the metal contaminated wafers, a vapor phase decomposition (VPD) in conjunction with atomic absorption spectrophotometry (AAS) was used to measure the contaminant level on the surface. The ellipsometer was used to measure the oxide layer thickness[91-93] in thermally oxidized wafers. These samples were then irradiated with UV and the change of effective lifetime was measured by Photo-conductive decay (PCD) method[94-97].

3.3.1 Spectroscopic Determination of Contamination Level

A Perkin Elmer model 5100 PC graphite furnace atomic absorption spectrophotometer (AAS) was used to identify the type and level of contaminants on the wafers surface. The spectrophotometer was calibrated by using the metal/nitric acid solution atomic spectroscopy standard (Fe, Cu, Ni, Zn and Al) from Perkin Elmer (PE). The linearity of calibration curve was better than 0.999.

The sequence of the wafer surface analysis steps for contaminated wafers is shown in Figure 3.7. The oxide layer on the contaminated wafers surface were removed by the (Hydrogen fluoride (HF)/hydrochloric acid (HCl)/hydrogen peroxide (H_2O_2) : 0.3/3/96.7(%) solution. One drop of this solution taken from the sample surface was then injected through a pipette into the Atomic Absorption Spectrometer (AAS) in which the contaminant types and levels were analyzed. The metal contamination was measured as L_m (atoms/cm^2) using the following equation

$$L_m = [\, Z \times 10^{-9} \,][\, \frac{V}{1000} \,][\, \frac{N_A}{m} \,][\, \frac{1}{A} \,] \tag{3.4}$$

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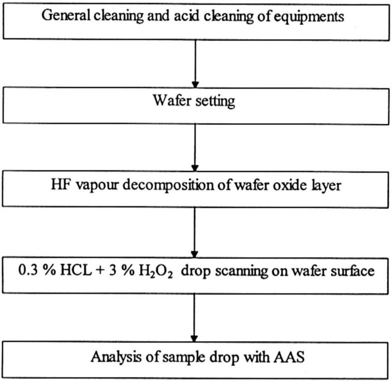

Figure 3.7 : Wafer surface analysis procedure

Z is the metal contamination level in the droplet; *V* is the total sample volume used in the AAS (μℓ); N_A is the Avogadro constant; *m* is the molecular weight of the element analyzed and *A* is the area of the wafer being scanned by the $HF/HCl/H_2O_2$ droplet.

3.2.2 Measurement of Oxide Layer

The oxide thickness was measured by a AutoEL IV ellipsometer (Rudolph Research Corp., USA). Before measuring the oxide layer thickness, the ellipsometer was calibrated with two standard samples from Rudolph Research Corporation which thicknesses were 394 ± 3 Å and 1136 ± 3 Å. The wafer was put on the automatic R-θ stage which positioned the wafer automatically so that any portion of the surface may be measured. A host computer was connected to the ellipsometer via a RS-232 communication cable as shown in Figure 3.8. The interface peripheral between AutoEL IV and host computer is the SECS (Semiconductor-Equipment and Materials-Institutes-Semiconductor-Equipment-Communications-Standard)

The AutoEL IV provides a wide variety of ellipsometric calculation routines for different layer configuration. The transparent, single-film configuration was used to determine the thickness of oxide layer. The wavelength of the light source, λ and angle of incidence, α were 6328 Å and 70° respectively and is shown in Figure 3.9, where NU (=1.462) and NS (=3.858) are the refractive indices of the oxide layer and silicon substrate.

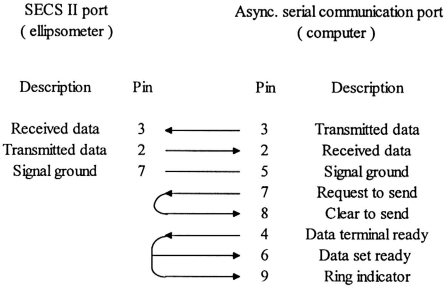

Figure 3.8 : Connections between the host computer and ellipsometer

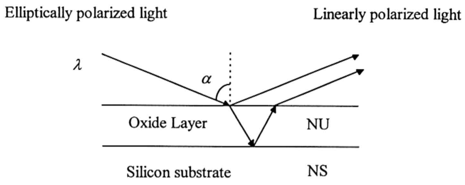

Figure 3.9 : Multiple reflections on the oxide-silicon substrate configuration

A program called the Ellipso-Map was used for the mapping of oxide thickness in which fifty points to cover the whole of the wafer surface were chosen to calculate the average oxide thickness of the wafer.

3.2.3 Lifetime Measurement

The effective minority carrier lifetime was measured by the laser-microwave photo-conductive decay technique (LM-PCD)[99-114] using the LIFETECH 2001 system (SEMITECH Co., Japan). The LM-PCD system used for the effective lifetime measurement is shown in Figure 3.10. The microwave source used to probe the excess carrier density has a frequency of 9.6 GHZ which is provided by a microwave oscillator. The reflected microwave power is detected by a microwave detector. The signal is amplified and converted into a voltage which is then analyzed by a computer. A laser diode at 904 nm and maximum power of 30 W is used to generate excess minority carrier. In this work, the laser output power was fixed at 14 W with the pulse-width at 150 ns. The reflected microwave power is dependent on the wafer conductivity. Hence, any excess minority carrier generated will change the conductivity and the microwave reflectivity. This system includes an ultra-violet (UV) light chamber with $\lambda = 253.7$ nm (4.9 eV) where the UV light affects only the wafer surface since its penetration depth into the wafer is less than 10 Å. The UV chamber incorporated six 8 watts UV lamps is shown in Figure 3.11. Both surfaces of wafer is irradiated with the UV in the chamber. This system was programmed to carry out the UV irradiation which was followed by the LM-PCD measurement of the effective lifetime, τ_{eff}.

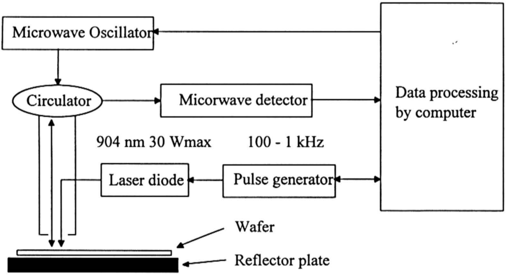

Figure 3.10 : Schematic of LIFETECH 2001 measurement system

Once the wafer is transferred from the polypropylene box into a cassette, the wafer is then loaded into the system by a robotic arm. The orientation of the wafer is corrected before it is being loaded into the UV chamber. The irradiation time is set between 1 to 999 seconds before the effective lifetime is measured by LM-PCD measurement technique. This procedure will be repeated for the accumulated UV-irradiation effect. The average effective lifetime of the five selected points which are equal distance from the center point of the wafer for every irradiation cycle is plotted against the UV irradiation time where the UV irradiation time is the accumulation of the time taken in individual UV irradiation cycle.

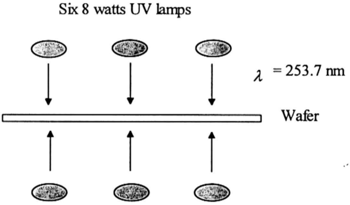

Figure 3.11 : Schematic of the UV chamber