CHAPTER THREE : EXPERIMENTAL TECHNIQUES

3.1   Preferential Etching

Preferential etching is an anisotropic etching process, which is also known as selective etching [1]. Its surface chemical activity is the rate-limiting step. This activity is affected by: crystallography, surface passivation, and surface electronic effects. The etch rate of such a process is kinetically controlled and can be written as
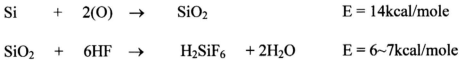
$$\frac{dn}{dt} = k A_1 C,$$

where k is the reaction rate constant, A_1 is the real surface area, and C is the etchant concentration.

Since the reaction rate constant, k, may vary locally in the presence of composition inhomogeneities and defects, dn/dt will correspondingly varies. These variations will produce a non-planar etched surface that reflects the distribution of chemical inhomogeneities and defects.

The formation of a non-planar etched surface, with the presence of dislocation pits or hillocks, arose mainly from the strain field associated with a dislocation and/or impurities segregated at a dislocation. This strain field produces surface potential between the site of a dislocation and the surrounding perfect crystal. The surface potential in turn causes a difference in the etching rate [14] between site of dislocation and surrounding perfect crystal. Therefore OISF can be delineated through preferential etching.

Preferential etching of semiconductors is electrochemical in nature. The process is controlled by two basic reactions: oxidation of silicon followed by the dissolution of oxide formed. Consequently, typical etchant contains a strong oxidizing agent such as nitric acid (HNO_3), and hydrofluoric acid (HF) that will dissolve the oxide.

In many situations the oxidation rate, dn/dt, at defect is greater than that of the surrounding silicon, this difference produces etch pits. When oxidation rate of the defect is lower than that of the defect-free region, mould-like features at defect sites are resulted. Etching mechanism of preferential etching is generally represented by 2-steps reaction [14]:

$$Si \quad + \quad 2(O) \quad \rightarrow \quad SiO_2 \quad\quad\quad\quad E = 14 kcal/mole$$

$$SiO_2 \quad + \quad 6HF \quad \rightarrow \quad H_2SiF_6 \quad + 2H_2O \quad\quad E = 6\text{~}7 kcal/mole$$

Silicon dissolution rate is determined by oxidation step. During preferential etching, byproduct such as nitrous acid with higher oxidation capability will be produced. Under this condition, rate determining step shifts to HF diffusion step.

Besides the byproducts, there are a few material parameters that affect etch rate. The etching rate differed between the defective and defect-free region [1]. Some of the parameters that affect etching rate are crystal orientation of silicon surface, type of dopant, dopant concentration, and composition of etchant used. Since holes are required for the oxidation of silicon, the etching of an n-type surface is accentuated in the presence of light; this behavior is attributed to the generation of

electron hole pair (EHP) however the effect of chemical etching to p-type silicon is small.

Table 3.1 : Etchants for Defect Delineation in Silicon [26]

Name of Etchant	Composition	Remarks
Sirtl and Adler (1961)	1 part concentrated HF 1 part CrO_3 (5M) 500g/liter of solution	~3.5µm/min etch rate; good on (111), poor on (001); faceted pits.
Secco-D'Aragona (1972)	2 parts concentrated HF 1 part $K_2Cr_2O_7$ (0.15M) 26g/liter of solution	~1.5µm/min etch rate; best with ultrasonic agitation, good for all orientations, particularly suitable for {001}; non-crystallographic pits.
Schimmel (1976)	HF : HNO_3 = 155 : 1	Applicable to p-type material.
Wright-Jenkins (1977)	2 parts concentrated HF 2 parts concentrated CH_3COOH 1 part concentrated HNO_3 1 CrO_3 (4M) 400g/liter of solution $Cu(NO_3)_2 3H_2O$ (0.14M) 33g/liter of solution	~1.7µm/min etch rate; ultra-sonic agitation not required; good on all orientations; faceted pits; good shelf life.

Table 3.2 : Composition of Preferential Etchant Used in This Study

Chemicals	HF	HNO_3	CH_3COOH	DI-Water
Volume	1 part	13 parts	3 parts	4 parts
% Volume	4.8%	61.9%	14.3%	19.0%

Table 3.1 showed etchants that are generally used in defect delineation. The etchant used in this project consists of hydrofluoric acid, nitric acid, acetic acid (CH_3COOH) and deionized water (DI water). Its composition is given in Table 3.2.

Etchant used was prepared by mixing all chemicals at given ratio. Two minutes etchant seasoning was carried out using 23 pieces of 6" wafers (1 basket). Activity of the etchant is known to deteriorate over time therefore etching rate has to be determined whenever etchant is being used. This etchant is used because it does not contain Cr that is harmful to environment. It is also favorable compared to Schimmel etchant because the presence of acetic acid acts as diluent that controls etching rate.

To determine etching removal of wafers with different crystal orientation, two types of wafer were used. The properties of etched wafers used are summarized in Table 3.3. 5" wafers used were grown by Czochralski method and these wafers were sliced from the middle portion of the boule used. These wafers were doped with Boron to obtained resistivity ranged of $14.0\Omega cm\sim16.0\Omega cm$. Wafer surface orientation was confirmed by X-Ray Diffraction method after slicing. Both surfaces of (100) and (111) wafers were etched using mix acids before used.

Table 3.3 : Properties of Wafer Used for Etching Rate Determination.

No	Properties
1	Czochralski grown 5" diameter wafer, p-type (Boron), 14.0 – 16.0Ωcm, (100) surface orientation, both surface etched.
2	Czochralski grown 5" diameter wafer, p-type (Boron), 14.0 – 16.0Ωcm, (111) surface orientation, both surface etched.

Wafer thickness was measured using digital dial gauge with resolution of 1μm, before and after preferential etching at predetermined time and intervals. Etching rate is given by the gradient of the graph shown in Figure 3.1. Surface removal is half of thickness change obtained because etching rate for both surfaces is presumed to be even.

Figure 3.1 : Etching Rate Determination
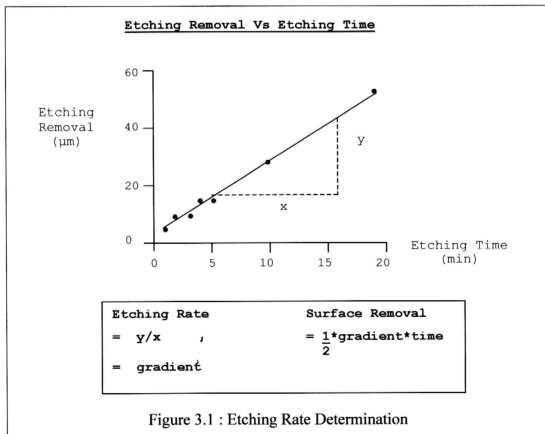
3.2   Atomic Force Microscopy [28, 25]

Atomic Force Microscope, AFM, is a member of Scanning Probe Microscope (SPM) family. SPM functions by positioning a very finely pointed tip extremely close to the surface of the sample. It is so close that in fact, the interaction between single atom on the tip and atoms of the sample occurs without direct contact taking place. It is also sensitive enough to trace out the contours of single surface atoms on the sample.

This interaction result may be a tiny current that flows between the gap and surface, or a variety of minute forces related to van der Waals, thermal, magnetic, electrical, optical and other properties of the sample. Although extremely small, such effects can be measure as the tip is moved point by point over the surface. In order to position the probe with such precision, SPM take advantage of the piezoelectric properties of ceramic materials, such as lead zircornate titanate (PZT).

Variation in SPMs depends on the design and function of the probe itself. AFM, which works well with insulating samples, measures atomic interactions relating to surface van der Waals forces. Its construction is similar to Scanning Tunneling Microscope (STM), with the important exception that it does not require the flow of a tunneling current for the signal.

AFM is capable of measuring tiny forces that exist by virtue of van der Waals, resonant exchange, electrostatic, and magnetic interactions between atoms of the

tip and atoms of the sample. Although very small, these forces are large enough to push the tip away, provided it is mounted on a flexible, highly compliant cantilever.
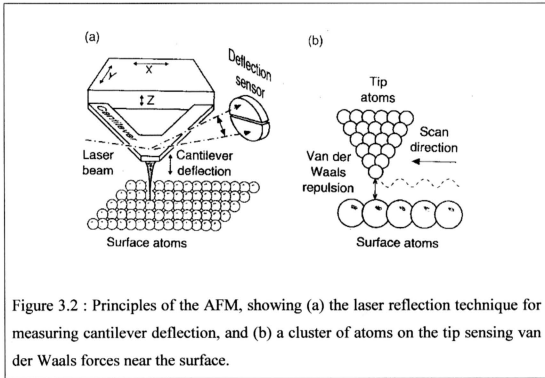

Figure 3.2 : Principles of the AFM, showing (a) the laser reflection technique for measuring cantilever deflection, and (b) a cluster of atoms on the tip sensing van der Waals forces near the surface.

Figure 3.2 shows the typical configuration of an AFM. The tip is fastened to a flexible cantilever, which in turn is mounted to piezoelectric drivers for X, Y, and Z movements. Often the tip and cantilever are fabricated concurrently from the same material, which typically is silicon, silicon dioxide (SiO_2) or silicon nitrite (Si_3N_4).

At a given point over the sample, atomic level interactions may repel or attract atom clusters of the tip and push it away, or pull it towards the surface. The vertical motion is sensed by observing the deflection of a narrow laser beam, which is reflected from the back of the cantilever.

Van der Waals forces are generally repulsive, provided the tip is not too closed to the surface. These begin to push against the tip as it approaches, resulting in a small upward bow of cantilever. The cantilever bends more over elevated points on the samples, and less over depressions. In this way, it is possible to map out roughness point-by-point across the surface without ever making direct contact. In practice, the tip and cantilever are usually raised and lowered to maintain a constant gap, or cantilever deflection hence the Z-piezo voltage tracks the surface topography in an analogous way to the constant current mode of STM.

AFM can operate in either contact or non-contact modes, but cantilever oscillation (tapping) mode is the mode universally practiced (*Refer Figure 3.3*). Contact mode is a classical method that resolves topography by lowering a tip onto the surface. Non-contact mode operates by the tip typically sits 50 Å to 100Å above the sample, monitoring attractive rather than repulsive van der Waals forces. Non-contact mode requires a stiff cantilever that vibrates in kilohertz and changes in the oscillation frequency are used to determine topography.

Contact mode is generally more robust because the forces involved are larger, although it is more prone to inflict damage to the sample. Surface damage can be minimized using a hybrid of contact and non-contact approaches known as the tapping mode.
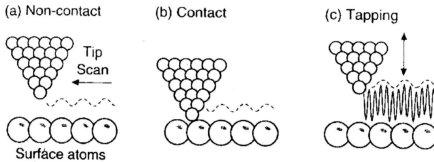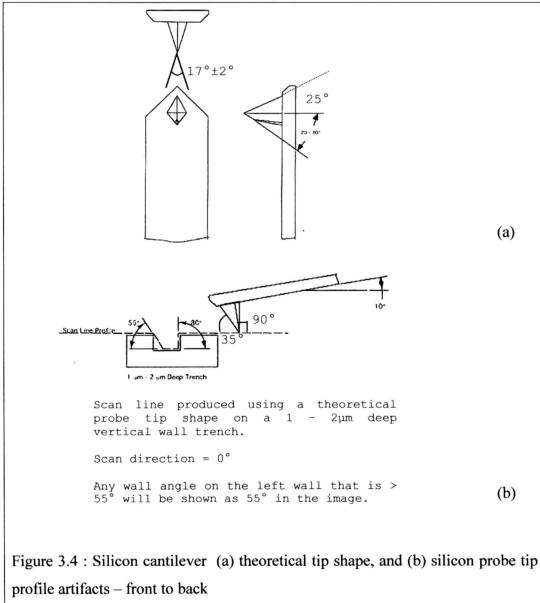
Figure 3.3 : AFM can be operated in either contact or non-contact modes, but cantilever oscillation (tapping) is more universally practiced.

In tapping mode, the tip is driven into vertical oscillation at the resonant frequency of the cantilever. It touches the surface only briefly at the extreme of each down cycle, so that physical contact with the sample is kept to a minimum. Here, the force at the tip is not measured directly as before, but is inferred from the way it changes the amplitude or resonant frequency of the cantilever. Cantilever oscillates like non-contact mode, but its typical amplitude is in the order of 200Å to 1000Å, thus tip taps or intermittently contacts rather than dragging across the surface.

Cantilever behavior is important for quality images and reproducible measurements. The tip, which interacts with the sample, will determine the type of information that can be extracted ultimately. Tip used in this project is made of silicon where a few hundreds of cantilevers with tips were etched electrochemically on the same piece of wafer. Figure 3.4 illustrates the theoretical tip shape of etched silicon probes and its tip profile artifact, when scanning is done parallel to cantilever length.

Scan line produced using a theoretical probe tip shape on a 1 – 2µm deep vertical wall trench.

Scan direction = 0°

Any wall angle on the left wall that is > 55° will be shown as 55° in the image.

Figure 3.4 : Silicon cantilever (a) theoretical tip shape, and (b) silicon probe tip profile artifacts – front to back

Theoretically, tips produced are symmetrical from side to side with a 17±2° half tone angle (*Refer top of Figure 3.4(a)*). Front-to-back, along the length of the lever, the tip is asymmetric (*Refer lower right of Figure 3.4(a)*). The substrates mounting angle, normally 10°, also affects the interaction of the tip shape with wafer surface (*Refer Figure 3.4(b)*).

Along the front edge of the tip, the half angle is nominally 25°. At the back edge of the tip the half angle is approximately 10°, with both of these numbers not

accounting for the tilt of the substrates. With the tip mounting and angle of the substrates taken into account, the front is 35° and the back is zero degree for perfect tip. From the side of the tip, the cross-section of the tip near the lever is approximately by an inverted "kite" shape. All of these subtleties arise from the etching process used to make the tip, which employs caustic solutions to perform wet anisotropic etching of the silicon.
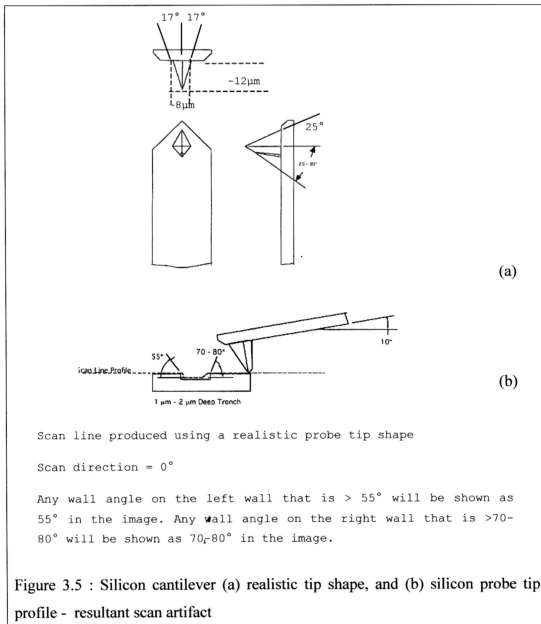
The best orientation of the sample for side wall's angle measurement is by the back edge of the tip (that which faces back towards the cantilever probe holder) to measure step angles as showed in Figure 3.4(b). By using back edge, step angles approaching 80° can be measured routinely, depending on the step of the height.

During measurement, we have to ensure that the area of measurement offers sufficient clearance so that other faces and edges of the tip and lever do not interfere with the measurement. This method does not work well with small openings of less than 5μm where, depending on the depth of the step, other edges of the tip could contact the other faces of the small opening. Wall angle measurements are best measured in open areas for these reasons.

Due to the nature of etching process that shapes the tip, there is often a short angled ridge near the highest point of the tip (*Refer Figure 3.5(a)*). The exact length of the ridge varies but rarely exceeds 0.5μm in total length. It is inclined steeply, so that for reasonably flat surfaces only the highest point interacts with the surface. Depending on the tip in use, sample features of approximately 0.5μm

in height can begin to produce artifacts of an apparent shallow slope over scan fields of larger than 1–2μm.

For realistic probe tip shape, when the trench is scanned in direction parallel to cantilever, any wall angle on the left wall that is more than 55° will be shown as 55° in the image. For the same trench scanning direction, any wall angle on the right wall that is more than 70°-80° will be shown as 70°-80° in the image.

(a)

(b)

Scan line produced using a realistic probe tip shape

Scan direction = 0°

Any wall angle on the left wall that is > 55° will be shown as 55° in the image. Any wall angle on the right wall that is >70-80° will be shown as 70°-80° in the image.

Figure 3.5 : Silicon cantilever (a) realistic tip shape, and (b) silicon probe tip profile - resultant scan artifact

AFM (Digital Instruments Nanoscope III D5000) has been used to characterize the shape and dimension of the OISF. The tips used in this work were fabricated from a single silicon substrate consisting of 387 etched silicon cantilever tips (TESP, Digital Instruments). The range of their resonant frequency, spring constant and radius of curvature were 264-328kHz, 28-54N/m and 5-10nm, respectively.

OISF measurements were carried out in air using Tapping Mode^{TM} of AFM, in which the atomic force applied was less than 1×10^{-10}N. The tip scanning direction varies according to wafer type and scanning purposes. Observation of each tip used was not done. Any discussion related to tip size and shape was referred to the standard realistic shape and profile given in Figure 3.5 [28]. Sample scanning parameters are given in Table 3.4.

Table 3.4 : AFM Settings for Sample Scanning in This Study.

No	Parameters	AFM Setting	
		Big Area Scanning	**Small Area Scanning**
1	Scan size	40μm x 40μm	20μm x 20μm
2	Scanning angle	(100) : 45°	(100) : 45°
		(111) : 0°	(111) : 0°
3	Scan sample	512	256
4	Scanning Mode	Tapping Mode^{TM}	Tapping Mode^{TM}
5	Scan rate	0.2 – 1.0 Hertz	0.2 – 1.0 Hertz
6	Z-limit	110V - 440V	110V - 440V
	Remarks	*For OISF length and width measurement*	*For OISF depth measurement (Refer Appendix B)*