Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen

NJIT
New Jersey's Science &
Technology University

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

A SILICON KNIFE
DESIGN AND FABRICATION

by
Mingli Wang

In this thesis, the design and fabrication of a silicon knife is described. The device design is based on the principle of oxidation sharpening.

The knife is made from a silicon wafer and can be made to be any chosen length up to 150 mm. It was made with the same basic procedures used in semiconductor chip manufacturing. This type of processing/manufacturing results in a knife with a high degree of sharpness and smoothness compared with existing knife technology.

The knife fabrication plan combines IC processing, techniques including anisotropic and isotropic etching of silicon, plasma dry etching and chemical etching dry oxidation, and KOH etching.

A SILICON KNIFE
DESIGN AND FABRICATION

by
Mingli Wang

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Electrical Engineering

Department of Electrical and Computer Engineering

May 1995

APPROVAL PAGE

A SILICON KNIFE DESIGN AND FABRICATION

Mingli Wang

Dr. R.B.Marcus, Thesis Advisor — Date
Research Professor of Electrical and Computer Engineering, NJIT

Dr. William N.M. Carr, Committee Member — Date
Professor of Physics, NJIT
Professor of Electrical and Computer Engineering, NJIT

Dr. Durgamadhab Misra, Committee Member — Date
Assistant Professor of Electrical and Computer Engineering , NJIT

BIOGRAPHY

Author: Mingli Wang

Degree: Master of Science in Electrical Engineering

Date: May 1995

Undergraduate and Graduate Education:

- Master of Science in Electrical Engineering,
  New Jersey Institute of Technology, New Jersey, 1995

- Master of Science in Optical Engineering,
  Huazhong University of Science and Technology, Wuhan, China, 1990

- Bachelor of Science in Solid State Engineering,
  Huazhong University of Science and Technology, Wuhan, China, 1983

Major: Electrical Engineering

This thesis is dedicated to my husband, my son and my mother

ACKNOWLEDGMENT

The author wishes to express her sincere gratitude to her thesis advisor Dr. R.B. Marcus for his continuing guidance, inspiration, and encouragement during the entire course of this thesis.

Special thanks to Professors William N. Carr and Dugramadhab Misra for serving as members of the committee.

The author would also like to express her appreciation to her friends in NJIT who have given her kindly assistance. Especially she thanks Dr. Xiaoyi Gu, Yongxia Zhang, Yawei Zhang and Joe Xu.

The author is especially grateful to Michael Grieco, Lab manager of the Microelectronics Research Center at NJIT, John Koons and Ken O'Brien for their invaluable guidance and foresight throughout this thesis. Without their cooperation, this research could never have been completed.

TABLE OF CONTENTS

Chapter	Page
1. INTRODUCTION	1
1.1 Introduction	1
1.2 Background of Thesis	2
1.3 Chapter Synopsis	3
2. PRINCIPLE OF MICROTOME KNIFE	4
2.1 Introduction	4
2.2 Geometry of Microtome Knife	5
3. DESIGN OF SILICON KNIFE	7
3.1 Design of Silicon Knife Process	7
3.2 Design of Silicon Knife Geometry	8
4. FABRICATION PROCEDURE OF SILICON MICROTOME KNIFE	11
4.1 Processing Sequence	11
4.2 Fabrication Procedure Description	12
5. CUTTING TEST OF THE ULTRASHARP SILICON KNIFE	37
5.1 Cutting in General	37
5.2 Cutting Test Experiments	38
6. SUMMARY AND CONCLUSION	42
6.1 Ultra-sharp knife	42
6.2 Improving Strength of Knife	42
APPENDIX A	44
APPENDIX B	47
REFERENCES	48

LIST OF FIGURES

Figure **Page**

1.1 SEM Photo of Atomically-Sharp Silicon Knife Edge Recently Fabricated at NJIT, 68,000X.......... 1

1.2 Atomically Sharp Silicon Tip Made by Oxidation Sharpening. The Same Principle Is Used to Make the Silicon Knife.......... 2

2.1 Illustration of Relative Positions of Knife and Sample Showing Clearance Angle α, Knife Angle β, and Knife Bisector x---x.......... 6

3.1 Cross Section of Silicon Knife.......... 9

3.2 A Perspective View of the Silicon Knife.......... 9

3.3 An Array of Silicon Knives Positioned on the Silicon Wafer.......... 10

4.1 Growth of Thermal Oxide.......... 14

4.2 Diagram of Photolithography Process.......... 15

4.3 Sample after Developing the Photoresist.......... 15

4.4 Sample after Patterning Oxide.......... 17

4.5a Sample after Directly Isotropically Etching Silicon without First Anisotropic Etch.......... 18

4.5b Sample after Sharpening I.......... 18

4.6a Sample Anisotropically Etching, then Isotropically Etching Silicon.......... 19

4.6b Sample after Sharpening II.......... 19

4.7 SEM Photo after Anisotropically Plasma Etching Silicon. 35,000X.......... 20

4.8 Sample after Anisotropically Plasma Etching Silicon.......... 20

4.9 Sample after isotropic etch and removing oxide.......... 22

4.10 Diagram of Very Sharp Knife Edge after Dry Oxidation.......... 24

4.11 SEM Photo of Very Sharpen Knife Edge 30,000X.......... 25

4.12 Sample after Growth of Thin Oxide.......... 26

LIST OF FIGURES
(Continued)

Figure **Page**

4.13 Sample after Deposition of Silicon Nitride 27

4.14 Sample Using Shipley Photoresist Which Does not Cover the Knife Edge 28

4.15 Sample with Special Photoresist Which Covers the Knife Edge 29

4.16 Photolithographic Process Using Mask#2 30

4.17 Sample after Developing Photoresist 32

4.18 Sample after Patterning Silicon Nitride and Oxide 33

4.19 Sample after KOH etching 34

4.20 Sample after Strip the Silicon Nitride and Oxide 35

4.21 SEM Photo of Result after 3.5 Hours KOH Etching 500X 35

4.22 SEM Photo Showing Undercutting after KOH Etching 36

4.23 Cross_section of Single Knife 36

5.1 Cutting Experiment 38

5.2 Broken Silicon Knife Edge 39

5.3 (a) Before the Knife was Blunt. (b) After the Knife was Blunt 40

5.4 Two Views at 5000X of 4 Cuts Made More Then 1.5μm Deep into the Outer Surface of the Human Hair 42

LIST OF TABLES

Table		Page
4.1	Wafer Cleaning Parameters	13
4.2	Steam Thermal Oxidation Parameters	14
4.3	Photolithographic Process Parameters	16
4.4	Anisotropic Plasma Etching Parameters	21
4.5	Isotropic Etching Parameters	23
4.6	Dry Thermal Oxidation Parameters	24
4.7	Silicon Nitride Deposition Parameters	27
4.8	Special Photolithographic Process Parameters for Covering 5 μm High Knife	31
4.9	Silicon Nitride Plasma Etching Parameters	31
4.10	KOH Anisotropic Etching Silicon Parameters	32
4.11	Silicon Nitride Stripping Parameters	34

CHAPTER 1

INTRODUCTION

1.1 Introduction

This thesis presents research on the fabrication of a silicon knife with on ultrasharp knife edge and very smooth knife surface. The method used to make this knife uses silicon fabrication procedures and oxidation sharpening to produce the sharp edge. This kind of ultrasharp silicon knife can be used to make microtome knives. The silicon knife edge produced in this research is shown in Figure 1.1, and has an ultrasharp knife edge and very smooth knife surface.

Figure 1.1 SEM photo of atomically-sharp silicon knife edge recently fabricated at NJIT. 68,000X

1.2 Background of Thesis

We are developing a silicon knife blade with an atomically-sharp cutting edge and with smooth knife surfaces based on an innovative procedure devised earlier for forming atomically-sharp silicon tips for electron emission[1]. This work on silicon tips is in turn based on research performed earlier at Bell laboratories on the thermal oxidation behavior of non-planar silicon surface[2].

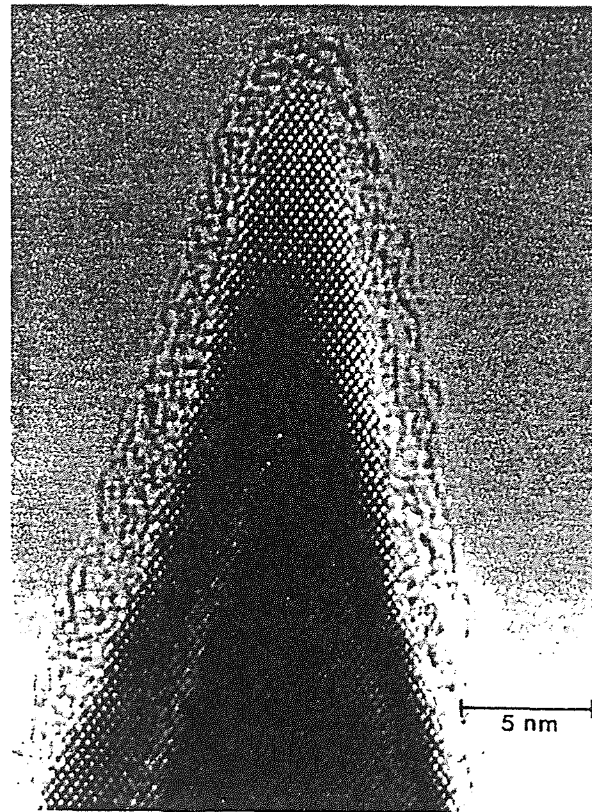


Figure 1.2 Atomically sharp silicon tip made by oxidation sharpening[1].
The same principle is used to make the silicon knife.

This pioneering work on thermal oxidation of non-planar silicon showed that regions of high curvature such as edges could be made to oxidize slower than flat surfaces and that these edges because progressively sharper as oxidation continued, finally becoming atomically sharp[3,4]. This research study concluded by proposing that the

mechanism was probably based on the impact of the stress configuration in the vicinity of the curved region on the oxidation kinetics within that region[2]. This observation was subsequently confirmed and then modeled by other, and is now a well-established feature of silicon oxidation. The same principle was applied more than 10 years later to the sharpen of tips of micron-high cones and pyramids of silicon, and procedures were developed[4] to form tips with controlled half-angles as small as 0.5-1.0 degrees and with radii of curvature of 0.5 nm as shown in Figure 1.2

1.3 Chapter Synopsis

This thesis is organized as follows: Chapter 1 introduces the silicon knife and the method of sharpening the silicon tip. Chapter 2 reviews the principle of operation of the knife which is used in microtomes. The silicon knife design is discussed in Chapter 3. The core of the thesis lies in Chapters 4 and 5, where the device fabrication is discussed. Chapter 4 focuses on the general fabrication sequence that was followed. Chapter 5 concentrates on methods used to test the newly-formed knife edge. A summary and conclusions are given in Chapter 6.

CHAPTER 2

PRINCIPLE OF ULTRASHARP KNIFE

2.1 Introduction

Microtomes were called cutting engines until 1839 when Chevalier introduced the word microtome[5]. Ultromicrotomy is the term used today to describe the technique of producing section of material thin enough for examination in the electron microscope. Ultramicrotomy is used to study all type of plant and animal tissue and other varied materials[6].

The two most important items in ultramicrotomy are the preparation of the specimen and the knife. The application that is the focus of this research is the microtome knife.

Both steel and glass knives are used in ultramicrotomy. The steel histology knife loose its sharpness after cutting a relatively few thin sections. Glass is a surpercooled liquid and the freshly broken edge of the glass knife is subject to molecular flow resulting in a rounding of the edge and therefore loss of sharpness. So the glass knife needs to be prepared on the day of use and not stored for any length of time.

A diamond knife is also used in ultramicrotomy. The crystalline structure of diamond provides a very sharp, stable edge of molecular thickness and of unsurpassed hardness, but the cost of a diamond knife is very high. Diamond knives vary considerably in performance and it is well worthwhile paying a little more to have one selected for a particular type of specimen.

This research develops a new knife which is made of silicon. The sharp edges of both the steel and diamond knives are made by honing, an abrasion process. The knife edge made in the current research is made by an etching and oxidation process, resulting in an edge that is far sharper and smoother than the edges of the steel or diamond knives.

2.2 Geometry of Microtome Knife

The common feature of these knives is a blade held at a small angle to the sample. The knife blade moves into the sample, and the newly-formed section is floated in a water trough. The relative positions of the knife blade and sample, clearance angle α and knife blade angle β are shown in Figure 2.1. The clearance angle α is typically fixed at 2-5°. The blade (cutting edge) is inclined at such an angle to the face of the sample (specimen block) that it is not quite parallel to the face. This angle is necessary in order to avoid the block face scraping the back of the knife after cutting a section. The net result is that as soon as a section is cut the block moves cleanly away from the back of the knife. In principle, the clearance angle should be as small as possible (provided the block does not come in contact with the back of the knife after the section is cut) because a knife with a large clearance angle will tend to scrape the sections instead of cutting them, which will result in chatter. Too large a clearance angle can also cause chipping of the knife. The chips thus produced may not be visible under the binocular microscope, but their effect in the form of lines perpendicular to the cutting edges shows up in the micrographs. The other important angle involved in sectioning is the knife angle (blade angle). The knife angle β is typically $45° \pm 10°$. The knife angle is critical for keeping the compression to a minimum knife angle. A smaller knife angle will result is decreased stress on the cutting edge of the knife, provided the optimal clearance angle is maintained. The blade is less likely to break when the angle γ ($\gamma = \alpha + 1/2\ \beta$) between the direction of the applied force F (the same as the direction of relative motion of the knife and the sample) and the line X---X is small.

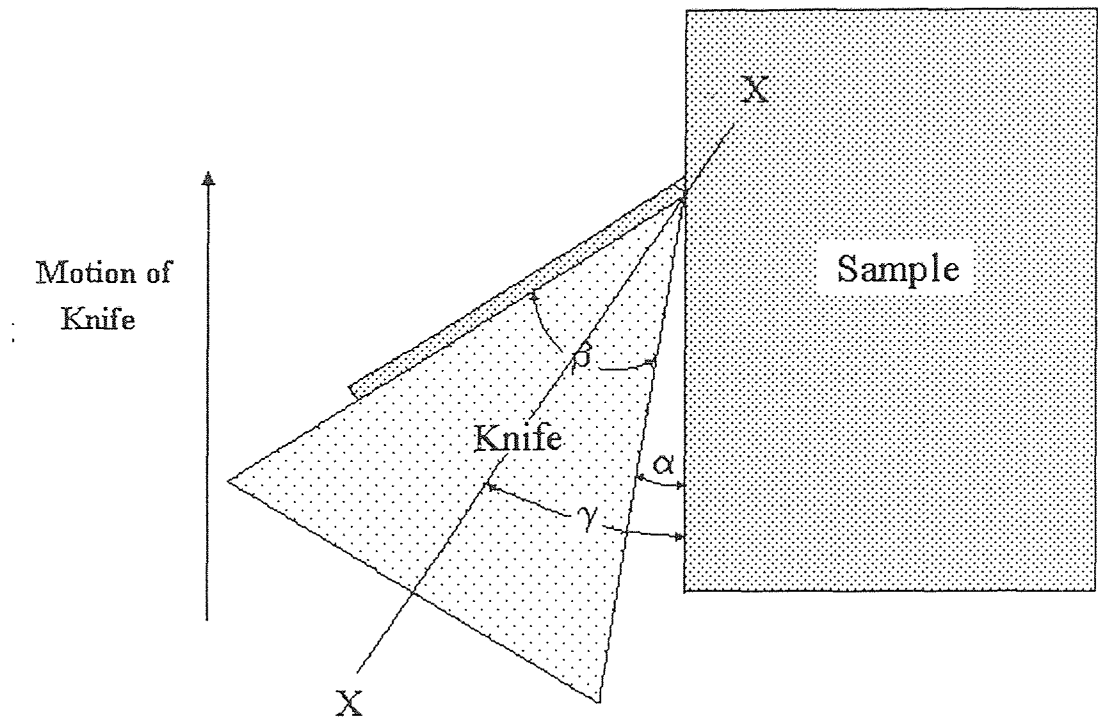


Figure 2.1 Illustration of relative positions of knife and sample showing clearance angle α, knife angle β, and knife bisector x---x.

CHAPTER 3

DESIGN OF SILICON KNIFE

The basic design of the silicon knife is dictated primarily by two requirements: functionality, and compatibility with IC processing techniques.

3.1 Design of Silicon Knife Process

The three main steps to forming a knife are: 1) make a "step" precursor structure that can be transformed into a knife edge; 2) form a knife edge from the step; and 3) separate individual knives from the wafer by etching. Steps 1) and 2) are based on the concept of "oxidation sharpening"[1,2,4] for forming an atomically-sharp edge of silicon. Step 3) is done by anisotropically etching through the wafer along {111} walls. In order to perform this etching step, silicon {110} wafers must by used and the features must be properly lined up (during the photolithography steps) along <110> directions.

In order to perform above three steps we will using the following process and measurement tools.

(1) Thermal oxidation which is used for growing an oxide film as the etching mask and sharpening the knife edge.

(2) Photolithography which is used for patterning the features.

(3) LPCVD (low -pressure chemical vapor deposition) for deposition of silicon nitride film as KOH (orientation) etch mask.

(4) Mixed acid (HNO_3:HF:CH_3COOH) to isotropically etch silicon to make the knife edge precursor shape.

(5) KOH orientation etching solution to anisotropically etch silicon.

(6) Plasma etch equipment to dry etch silicon, oxide and silicon nitride.

(7) Optical microscope to stude the samples after each step.

(8) Leitz thickness measurement equipment to measure the thickness of various film.

(9) Dektek step measurement equipment to roughly measure the height of step shape. This is a stylus instrument.

(10) SEM (scanning electron microscope) is a very important tool to study the sample after key step and to perform the cutting test.

3.2 Design of Silicon Knife Geometry

The design of the silicon knife is based on the microtome knife design as described above and in Figure 2.1 One side of the knife edge must be nearly vertical to avoid to scraping the sample, and the other side must be lowered in order to contain water for floating off a cut sample. The cross section of silicon knife is shown in Figure 3.1, and the overall geometry of the silicon knife is shown in Figure 3.2. Although β can be made quite small, the "effective knife angle " β' is significantly larger and dominates the value for γ. The effective knife angle β' depends on the ratio of the tip height **h** to the base **r**. From the Figure 3.1:

$$tg(\tfrac{1}{2}\beta') = \mathbf{r/h}$$

$$\beta' = 2\ \mathrm{arctg}\ (\mathbf{r/h})$$

In our research, we used the **r** $\cong$ 2 μm and the **h** $\cong$ 5 μm, then the $\beta' = 43°6$ and $\gamma = \frac{1}{2}\beta' + \alpha$ may therefore be as large as 25°-30°. If the blade is too fragile with these parameters then the blade can be made more durable either by altering the geometry (change **r** and **h**) or by adding thin coating of a hard material, or both.

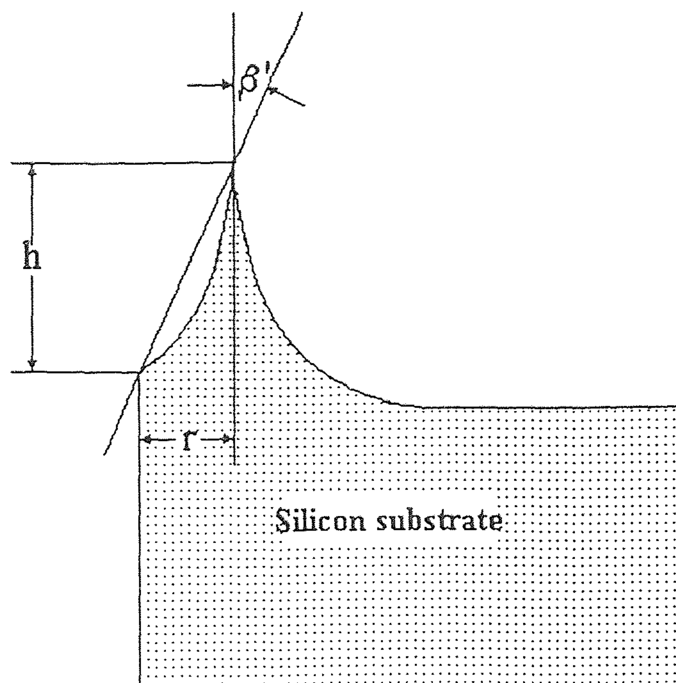


Figure 3.1 Cross section of silicon knife

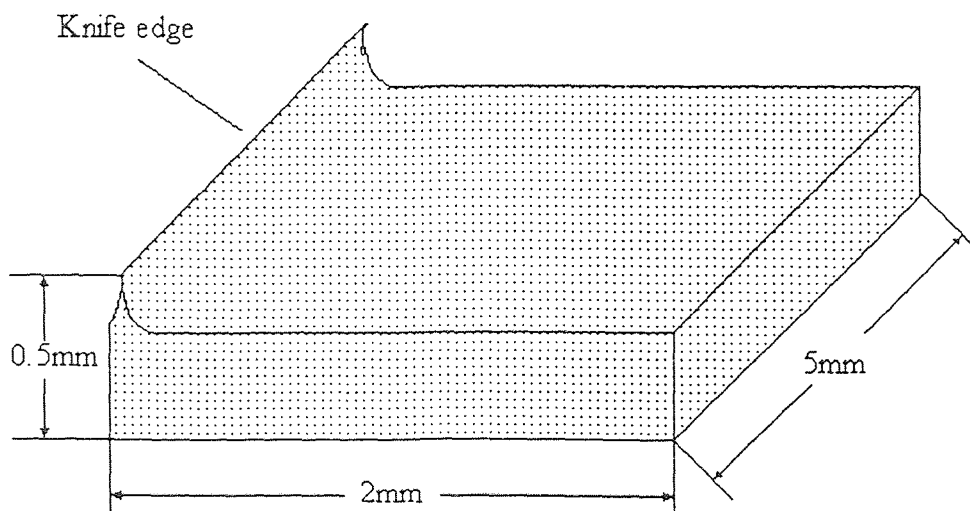


Figure 3.2 A perspective view of the silicon knife

The knife was designed with the dimensions shown in Figure 3.2: length = 5mm, width = 2 mm, and thickness = 0.5mm.

The array of silicon knives is shown in Figure 3.3. Making this silicon knife requires two photolithography steps, An oxide film is used as the first etch mask and a silicon nitride film is used as the second etch mask.

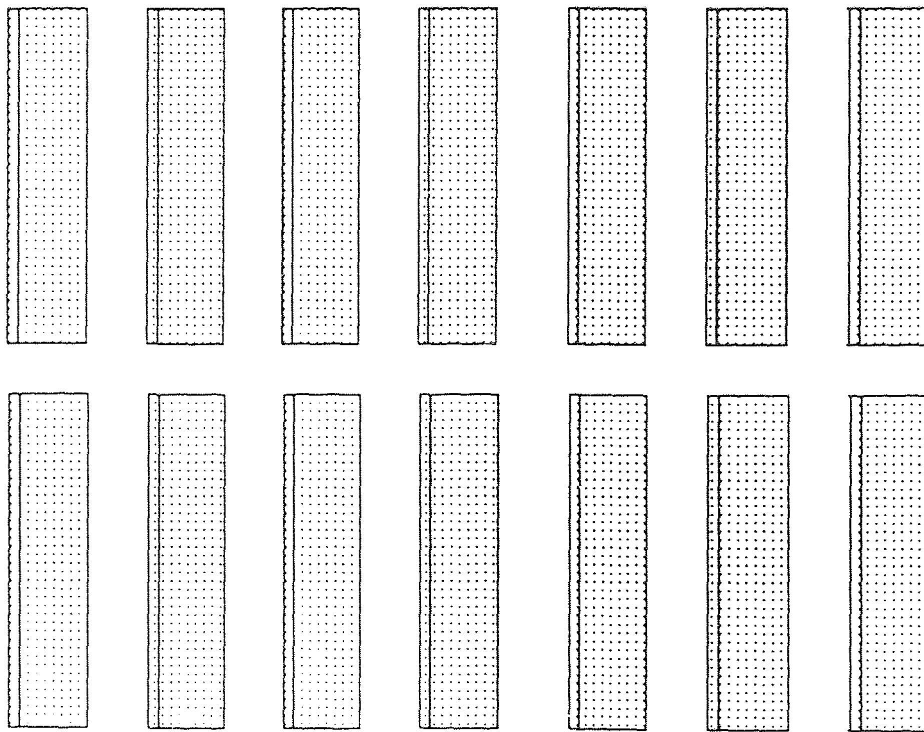


Figure 3.3 An array of silicon knives positioned on the silicon wafer

CHAPTER 4

FABRICATION PROCEDURE OF SILICON ULTRASHARP KNIFE

All of the fabrication work for this thesis was performed at the NJIT Microelectronics Research Center (NJIT MRC). The starting substrates were 4" , <110> n-type silicon wafers, resistitvity 10~20 Ω-cm.

4.1 Processing Sequence

The processing steps are illustrated in Figures 4.1-4.23. The details of the fabrication procedure will be discussed in section 4.2.

The processing sequence of the silicon ultrasharp knife can be summarized as follow:

1. Starting material: highly-doped <110> n-type silicon, 4" wafer.
2. Grow 0.4 -0.5 μm steam oxide.
3. Pattern oxide (10 μm features):
    - 3a. P-L (opaque features). (Mask #1)
    - 3b. Etch oxide (BOE).
4. Anisotropic etch silicon 0.3 μm:
    - 4a. Using plasma etching silicon.
    - 4b. Strip photoresist.
5. Isotropic etch silicon to a depth of 5 μm: (HNO_3:HF:CH_3COOH)
6. Remove oxide.
7. Oxidation sharpening:
    - 7a. Dry oxidation at 950°C (5 hours).
    - 7b. Strip oxide.

*. Repeat 7a and 7b several times until the knife edge is very sharp.

8. Deposit nitride:

8a. Dry oxidation at 950° 20 minutes.

8b. LPCVD Si_3N_4 at ~750°C. thickness ~2000Å.

9. Pattern nitride:

9a. P-L (opaque features). (Mask #2)

9b. Pattern nitride (plasma etch).

9c. Etch oxide (BHF).

9d. Strip photoresist.

10. Anisotropically etch silicon (KOH at 80°C, ~3 hours).

11. Strip silicon nitride and oxide:

11a. Strip silicon nitride (HPO_4, at 170°C, 23 minutes).

11b. Strip oxide (HF).

12. Separate silicon knives.

4.2 Fabrication Procedure Description

1. Starting material.

N-type silicon wafers oriented in the {110} crystallographic plane are used in this research. First, the silicon wafers are cleaned chemically to remove surface contamination. Aqueous mixtures of NH_4OH-H_2O_2, HCl-H_2O_2, and H_2SO_4-H_2O_2 are often used. These cleaning resolutions leave the wafer surface in a hydrophilic state due to the oxide formed by the peroxide. In a hydrophilic state, water will wet the wafer surface the energy of the water/oxide interface is very low. The chemicals are removed by a short immersion in dilute hydrogen peroxide clean followed by the hydrofluoric acid to remove the oxide. In this research, we used H_2SO_4-H_2O_2 to clean all wafers, then used 100:1 H_2O:HF to pre-clean the wafers before they go into the furnace. The cleaning parameters are shown in Table 4.1.

Table 4.1 Wafer cleaning parameters

Parameter	Value
H_2SO_4:H_2O_2	5:1
Temperature	110°C
Time (wafer in chemical)	10 minutes
H_2O:HF	100:1
Temperature	25°C
Time (wafer in chemical)	10 minutes

2. Grow 0.4 -0.5 μm steam thermal oxide.

In order to make the knife edge, first we need make the knife edge precursor shape; that is, we need to etch the silicon, using a SiO_2 film as the etch mask.

In order to protect the silicon during chemical etch, we needed an oxide thickness of 4000Å, and we used the steam thermal oxidation. The oxidation time needed was calculated (based on the oxidation thickness versus time curves for NJIT-MRC's thermal oxide) to be 40 minutes. The sample after thermal oxidation is shown in Figure 4.1. The steam oxidation deposition parameters are shown in Table 4.2.

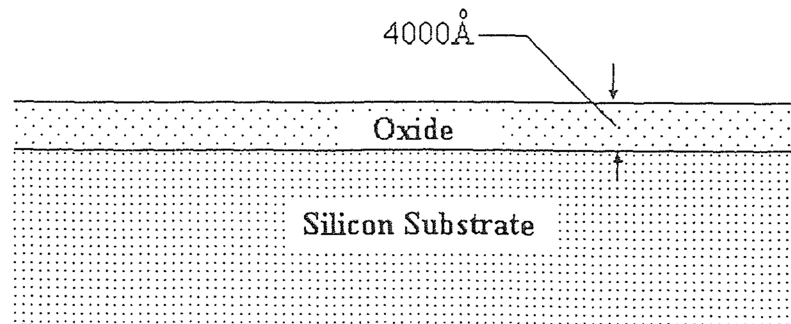


Figure 4.1 Growth of thermal oxide

Table 4.2 Steam thermal oxidation parameters

Parameter	Value
Tube Temperature	1050°C
Bubbler Temperature	98°C
Tube Oxygen Flow	7.5 SLM
Bubbler Oxygen Flow	750 sccm
Deposition time	40 minutes
Film Thickness	~ 4000Å

3. Pattern Oxide:

The SiO_2 is used as a mask to protect the silicon which we do not want etched. In order to perform this process, we used photolithography to pattern the oxide. We used NJIT-MRC's standard photolithography process. That is, we used a chromium/glass mask with ultraviolet (UV) light and a positive photoresist. A summary of the coat, bake and develop conditions is given in Table 4.3. Figure 4.2 shows the sample during exposure, and Figure 4.3 shows the sample after the resist is developed.

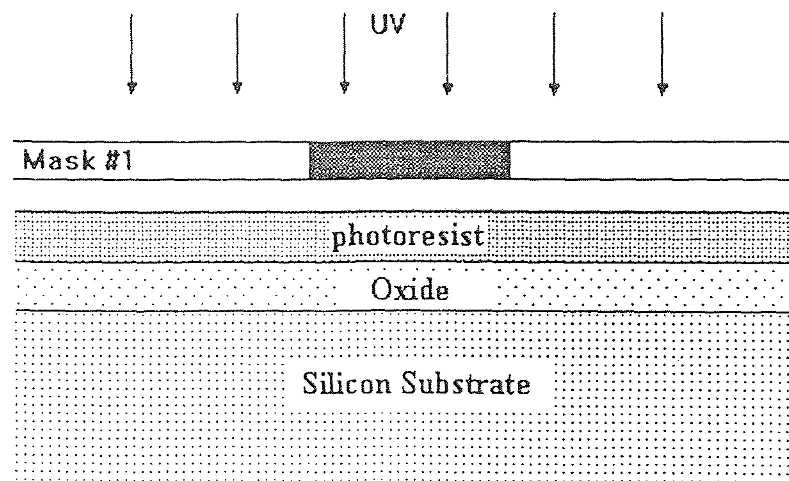


Figure 4.2 Diagram of photolithgraphic process

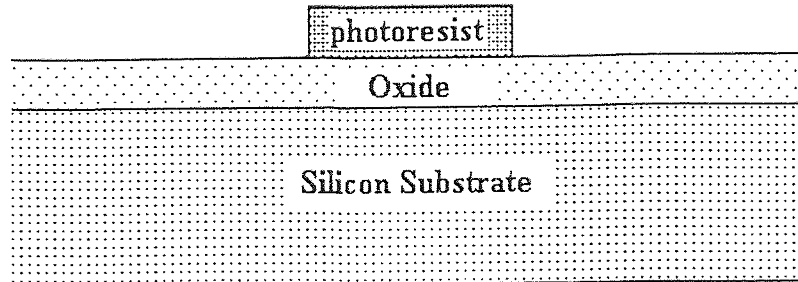


Figure 4.3 Sample after developing the photoresist

Table 4.3 Photolithographic process parameters

Parameter	Value
Vapor HMDS Temperature	135°C
Photoresist	Shipley 1813
Spin speed	4500 RPM
Spin time	20 seconds
Soft bake time/temperature	20 minutes/110°C (Oven)
Exposure power density	25 mW/cm^2
Exposure time	10 seconds
Developer	Shipley MF319
Developer time	30+15 seconds
Hard bake time/temperature	20 minutes/115°C (Oven)

After lithography we need to remove the oxide so the next step is to etch the oxide in 7:1 BOE. Immediately prior to the etch, the etch rate of the thermal oxide was measured on a test sample in order to precisely control the etch time. We did not want to

over-etch the oxide because over-etching oxide produces a small feature width, and the knife height will be shorter than we expect. Different temperatures cause a different etch rate. The etch rate of the thermal oxide in 7:1 BOE at a temperature of 25°C~27°C is around 1000Å/minute. For our sample, we need to grow about 4000Å SiO_2, but each wafer has slightly different thickness so after steam oxidation we must use the Leize optical machine to exactly measure the oxide thickness of each wafer. Then the required etch time can be easily be calculated. With a temperature of 26°C and an etch rate of 1000Å, the etch time is about 4 minutes in 7:1 BOE. After oxide patterning the sample is shown in Figure 4.4.

4. Anisotropic etch Si (plasma etch)~0.3μm.

Before the isotropic etching step, an anisotropic etch is needed to increase the height of the knife. Without anisotropic etch, after the oxidation sharpening , the knife height would be very short as shown in Figure 4.5a and 4.5b and the knife angles β and β' will be very large. Instead, when an anisotropic etch is first used, the result is shown in Figure 4.6a and 4.6b. The height of the knife shown in Figure in 4.6b is larger, and the effective knife angle β' is smaller.

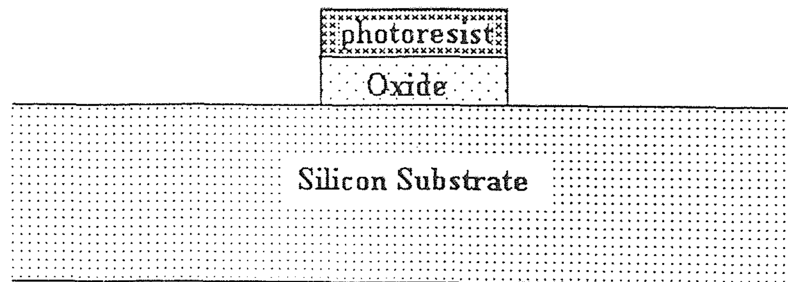


Figure 4.4 Sample after patterning oxide

In order to keep the oxide on the back side of the wafer, plasma etching was used to anisotropically etch the silicon.

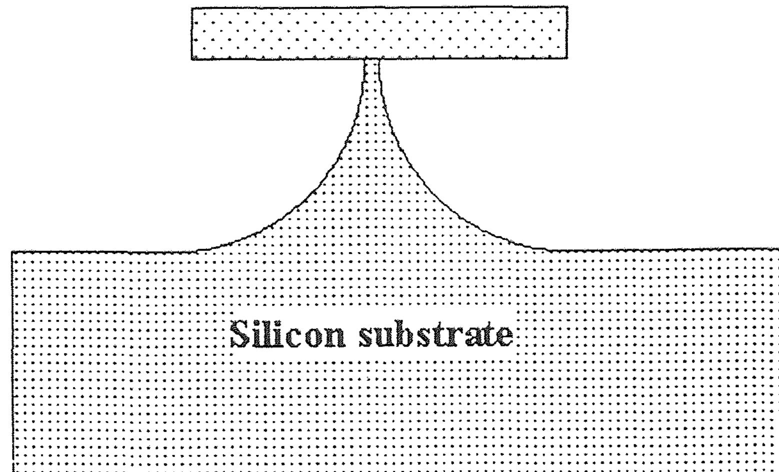


Figure 4.5a Sample after directly isotropically etching silicon without first anisotropic etch

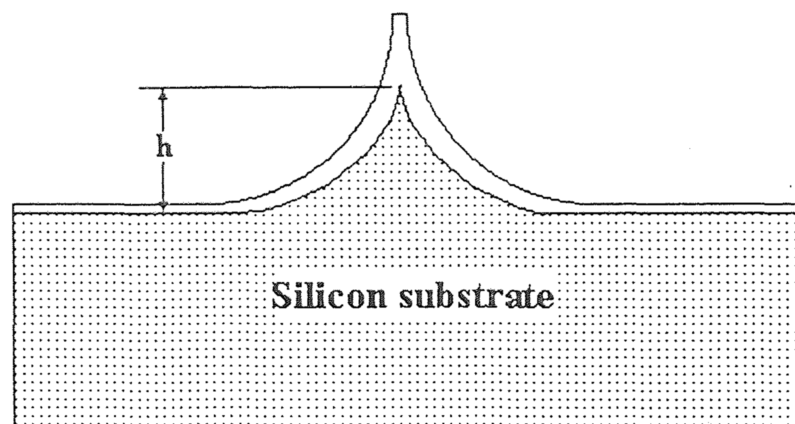


Figure 4.5b Sample after sharpening I

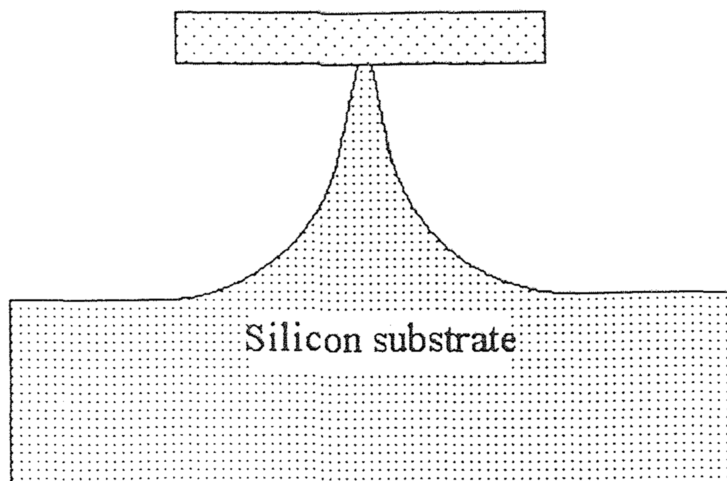


Figure 4.6a Sample after anisotropically etching, then isotropically etching silicon.

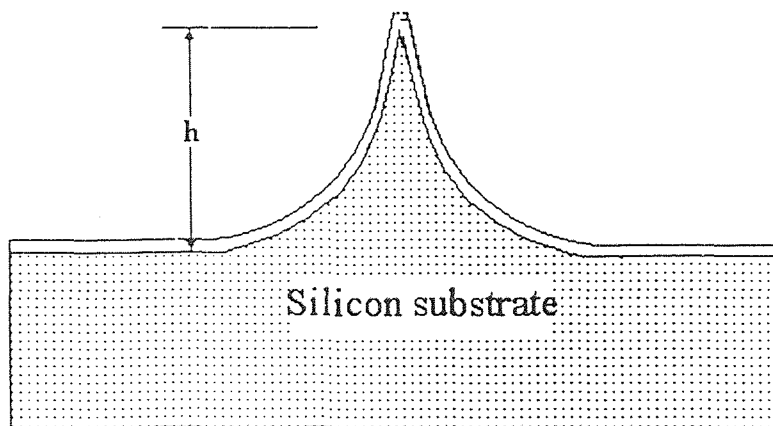


Figure 4.6b Sample after sharpening II.

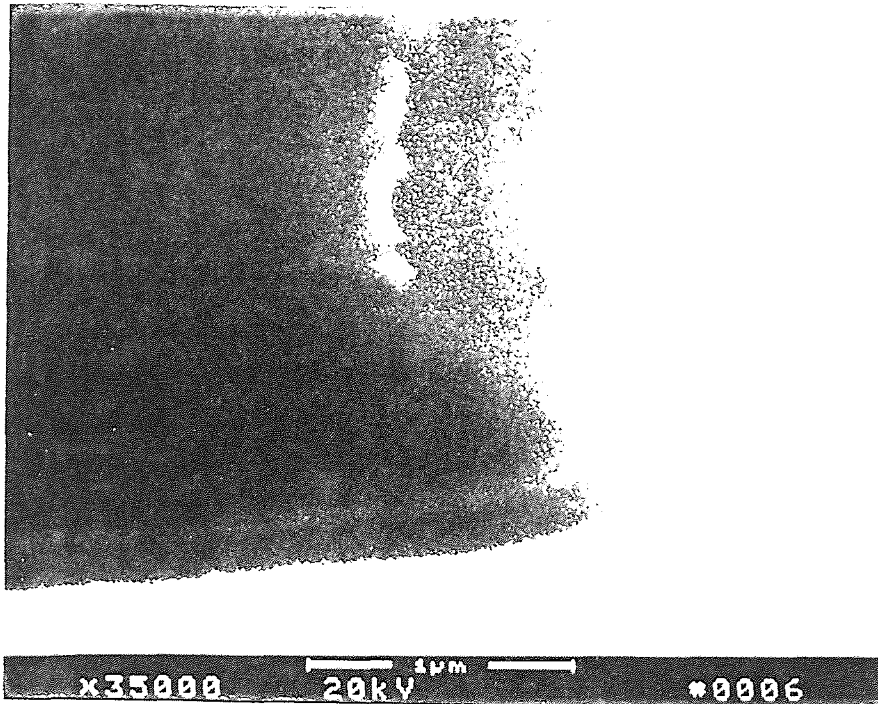


Figure 4.7 SEM Photo after anisotropically plasma etching silicon. 35,000X

The dry etch (plasma etch) was done in a Drytek DRIE-100 plasma etcher. When Si is etched with photoresist as a mask, etching is anisotropic, but when oxide is used a mask then the etching is isotropic. Because we need the oxide mask for chemically etching the silicon, a combination of both photoresist and oxide masks were used. After one minutes plasma etching, the result shown in Figure 4.7 is almost anisotropic and acceptable. A diagram of sample after plasma etching is shown in Figure 4.8. Then we strip the photoresist. A summary of the etch parameters is given in Table 4.4.

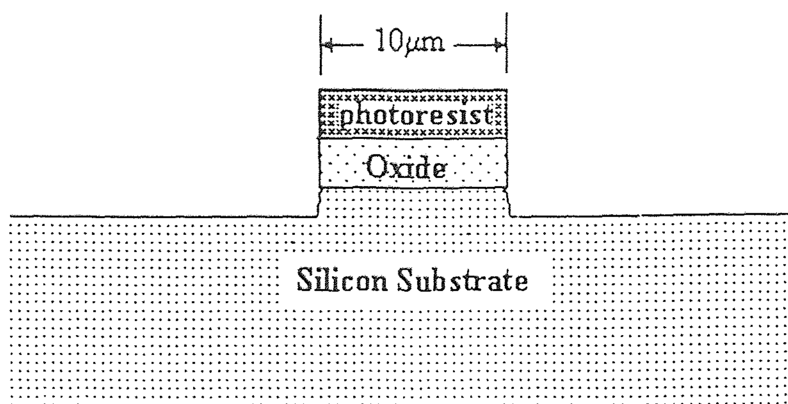


Figure 4.8 Sample after anisotropically plasma etching silicon

Table 4.4 Anisotropic plasma etching parameters

Parameter	Value
SF_6	50sccm
Freon 115	50sccm
Pressure	150mTorr
Power	400Watt
Temperature	25°C
Etch rate	~ 0.15μm/min
Etch time	2 minutes
Depth of etch	0.3μm

5. Isotropic etching silicon.

Wet isotropic etching using a mixture of nitric aid (HNO_3) and hydrofluoric aid (HF) is used to make the correct "precursor" shape for oxidation sharpening. The reaction is initiated by the HNO_3 which forms a layer of silicon dioxide on the silicon, and the HF dissolves the oxide away. The over all reaction is:

$$Si + HNO_3 + 6HF \longrightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O$$

Water can be used to dilute the etchant, but acetic acid (CH_3COOH) is preferred as a buffering agent, since it causes less dissolution of HNO_3 and thus yields a higher concentration of the undissociated species.

The mixture composition can be varied to yield different etch rates. On the other hand at low HF and high HNO_3 concentration, the etch rate is limited by the ability of the HF to remove the SiO_2 as it is created. In such etchant the etching is isotropic.

In this research, we want the etch rate to be slow and uniform, so volume the ratio of the chemicals used is HNO_3 : HF : CH_3COOH = 95% : 2% : 3%. At room temperature, the etch rate is about 0.25 ~ 0.3 μm per minute.

The disadvantage of chemical etching is that the etching is not uniform when etching is performed in the usual manner with the wafer flat in the bottom of a container. The features on the inside of the wafer etched slower than the features on the edge of the wafer. In order to get a more uniform and isotropic etch, some experiments were performed with different etching configurations. The arrangement that worked the best and gave acceptable results was where the wafer was mounted vertically and continuously agitated during etching. In order to produce atomically sharp edges, the tip should be very small before oxidation sharpening, preferably less than 0.4 ~ 0.5 μm. In this research, the feature width is L=10 μm, and etch time is about 17 ~ 20 minutes. Because the chemical etch rate is not very uniform, the sample must be inspected every 30 seconds at the end of a few minutes. A summary of silicon isotropic etch parameters is given in Table 4.5. The sample is shown in Figure 4.6a.

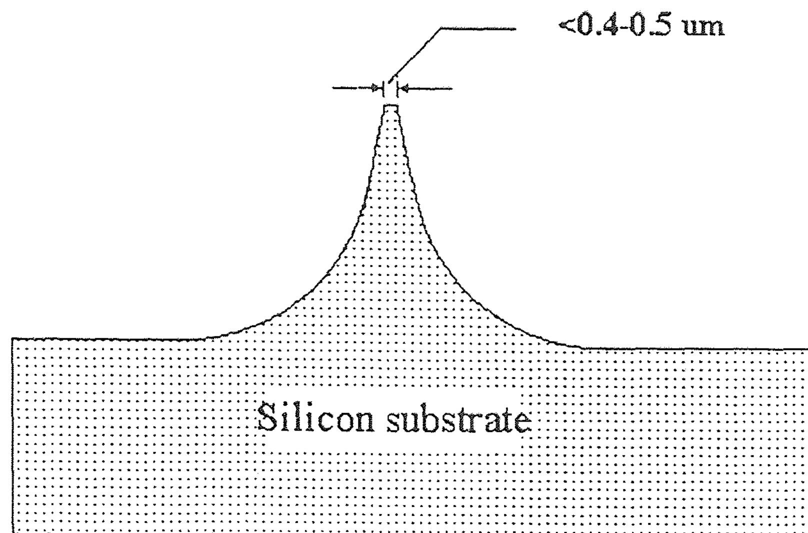


Figure 4.9 Sample after isotropic etch and removing oxide

6. Remove oxide.

The next step, we removed the oxide in 7:1 BOE for ~ 4 minutes. The diagram is shown in Figure 4.9.

7. Dry oxidation sharpen.

Oxidation sharpening occurs at a furnace temperature of 950°C and with an oxidation time of about 2 - 5 hours[2].

Table 4.5 Isotropic etching silicon parameters

Parameter	value
HNO_3:HF:CH_3COOH	95%:2%:3%
Etch rate	0.25 - 0.3 μm/minute
Temperature	room temp.
Etch time	18 ~20 minutes
Height **h**	4.6 ~5 μm

According to oxidation theory[8,9], since 1 mole silicon is converted to 1 mole silicon dioxide.

$$\frac{\text{Thickness of Si} \times \text{area}}{\text{Thickness of SiO}_2 \times \text{area}} = \frac{\text{Volume of 1 mole of Si}}{\text{Volume of 1 mole of SiO}_2}$$

$$\therefore \quad \frac{\text{Thickness of Si}}{\text{Thickness of SiO}_2} = \frac{12.06}{27.18} = 0.44$$

The thickness of silicon = (0.44) × (thickness of silicon dioxide). That is, to growth 1000Å of silicon dioxide, a layer of 440Å of silicon is consumed.

In step 6, the width of the tip is about 0.4 - 0.5 μm. Oxidation must proceed for a time long enough to consume 0.4 - 0.5 μm silicon. Dry oxidation must be repeated enough times to consume all silicon and make the edge very sharp. The appearance of the very sharp knife edge after dry oxidation is shown in Figure 4.10. A summary of dry oxidation parameter is shown in Table 4.6.

Table 4.6 Dry thermal oxidation parameters

Parameter	Value
Tube temperature	950°C
Tube oxygen flow	7.5 SLM
Deposition time	2-5 hour

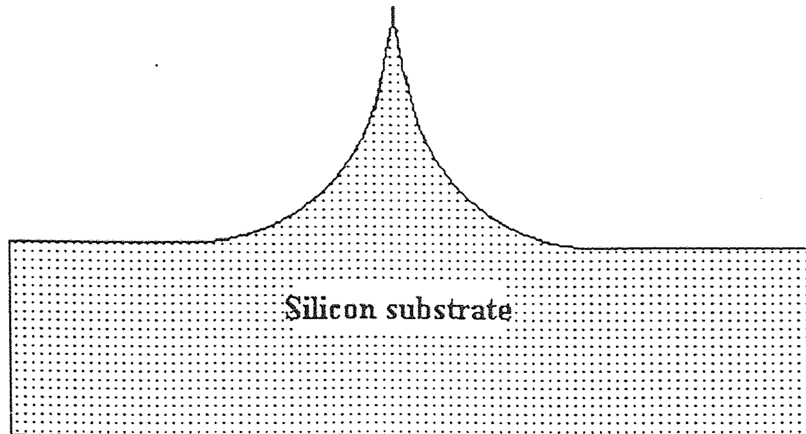


Figure 4.10 Diagram of very sharp knife edge after dry oxidation

8. Nitride deposition.

After the sharpening step, we need to separate the each knife. We use a KOH solution as an anisotropic etch to etch through the wafer and separate the knife. In order to protect the knife when the wafer is etched a long time in the KOH solution, nitride film is used as a mask because silicon nitride etches very slowly in KOH and prevents the underlying silicon from etching.

Before depositing the nitride film, we need to grow a very thin layer of oxide to decrease the stress of the nitride film. This is done using dry oxidation at temperature 950° C for 20 minutes. Figure 4.12 shows the sample after growing the thin oxide.

Silicon nitride was deposited by a CVD (atmospheric-pressure chemical vapor deposition) process which is used to form various insulator films on substrates surfaces through thermal decomposition of source materials in the vapor phase. The LPCVD (low-pressure chemical vapor deposition) films are of stoichiometric composition (Si_3N_4) with high density (2.9 to 3.1 g/cm^3). In LPCVD process dichlorosilane and ammonia react at

high density (2.9 to 3.1 g/cm^3). In LPCVD process dichlorosilane and ammonia react at reduced pressure to deposit silicon nitride at temperature between 700°C and 800°C. Thirty-eight minutes are needed to grow 2000Å Si_3N_4. film. The reaction is:

$$3SiCl_2H_2 + 4NH_4 \longrightarrow Si_3N_4 + 6HCl + 6H_2$$

A summary of silicon nitride deposition parameters is shown in Table 4.7 and an illustration of the sample after this step is shown in Figure 4.13.

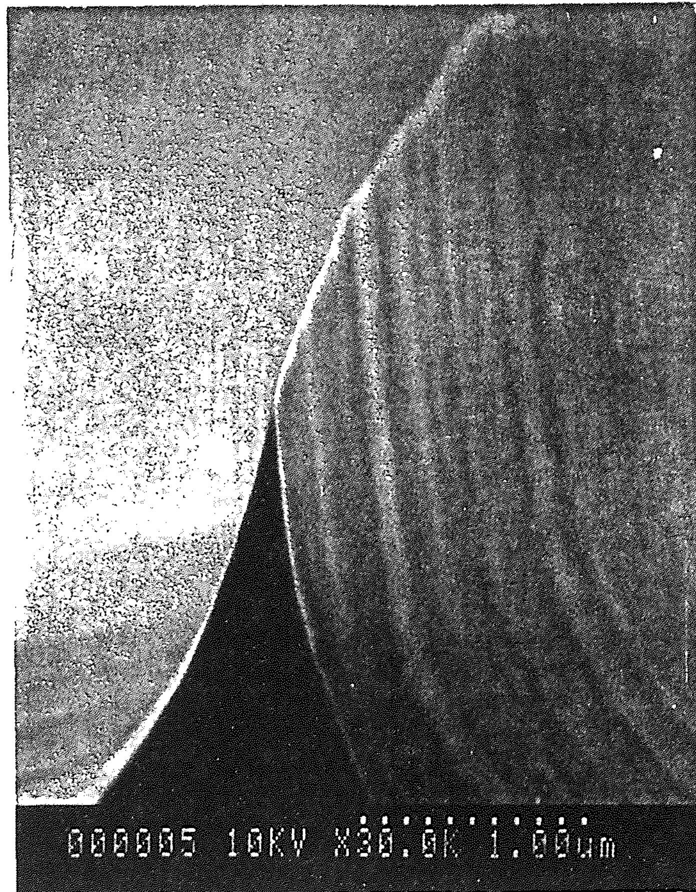


Figure 4.11 SEM photo of very sharp knife edge 30,000X

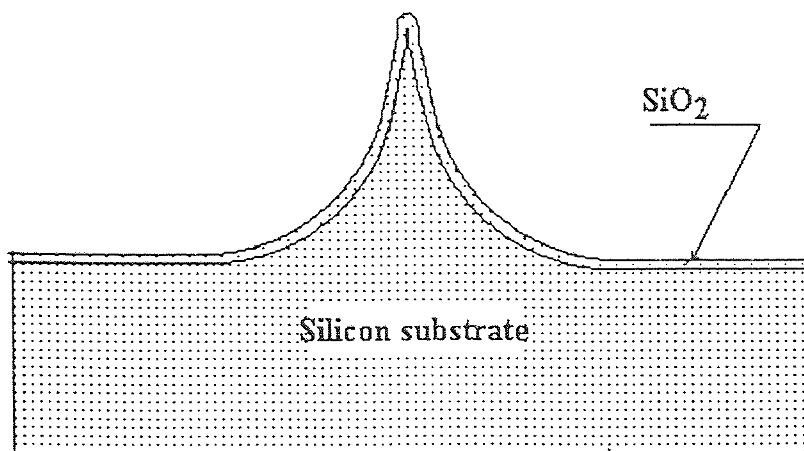


Figure 4.12 Sample after growth of thin oxide

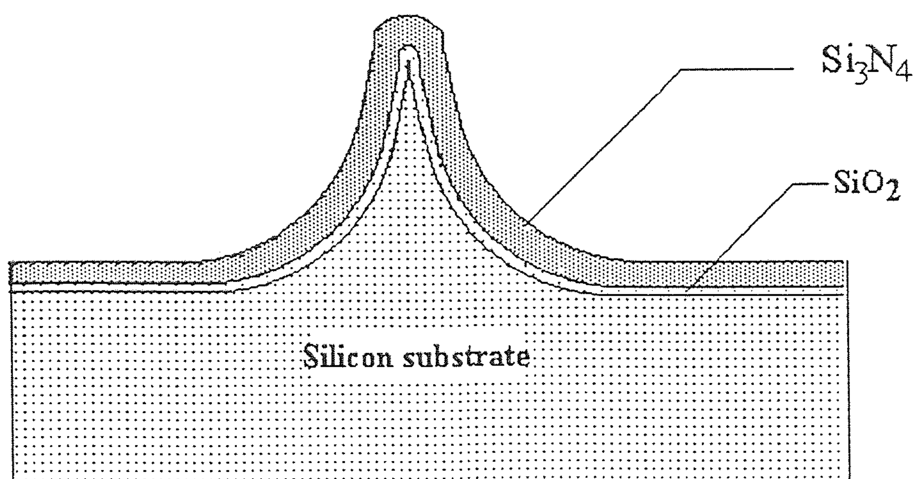


Figure 4.13 Sample after deposition of silicon nitride

Table 4.7 Silicon nitride deposition parameters

Parameter	Value
NH_3	120 sccm
Pressure	400 mTorr
Temperature	775°C
Deposition rate	50~60 Å/minute
Deposition time	38 minutes
Film Thickness	2000Å

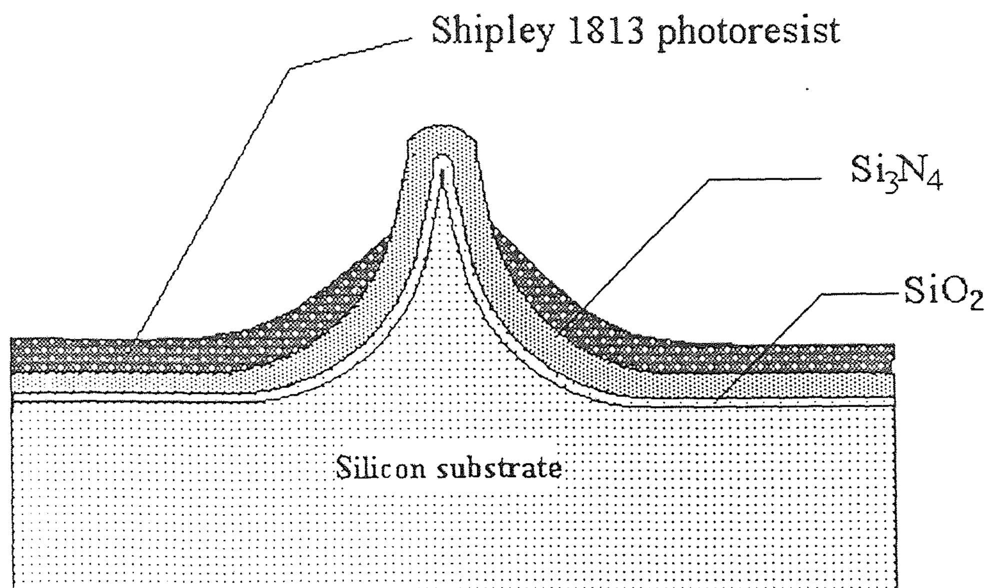


Figure 4.14 Sample with Shipley photoresist which does not cover the knife edge

9. Patterning the silicon nitride as mask for KOH.

The next step is photolithography for the nitride mask 2. This is a problem because the knife edge is as high as 5 μm, and the standard 1.5 μm photoresist does not cover the knife edge as shown in Figure 4.14. After doing some experiments it was found that the resist thickness needed to be thicker than the height of the knife, and this was done with AZ 4903 resist plus thinner (3:1). Spin rates of 2000, 2500, and 3000 RPM gave

photoresist thickness of 7.0µm, 6.7µm, and 6.2µm respectively. The thickness is higher than the height of the knife edge so that it can protect the knife edge as shown in Figure 4.15. The second photolithographic process using mask#2 is shown in Figure 4.16 and sample after developing photoresist is shown in Figure 4.17. The special photolithographic process parameters are shown in Table 4.8.

In the next step we need to pattern the silicon nitride feature. In order to protect the silicon nitride on the back surface, plasma etching was used for etching silicon nitride. The silicon nitride etching was done in a Drytek DRIE-100 plasma etcher. The wafers were etched for 5 minutes. A summary of the silicon nitride plasma etch parameters are shown in Table 4.9.

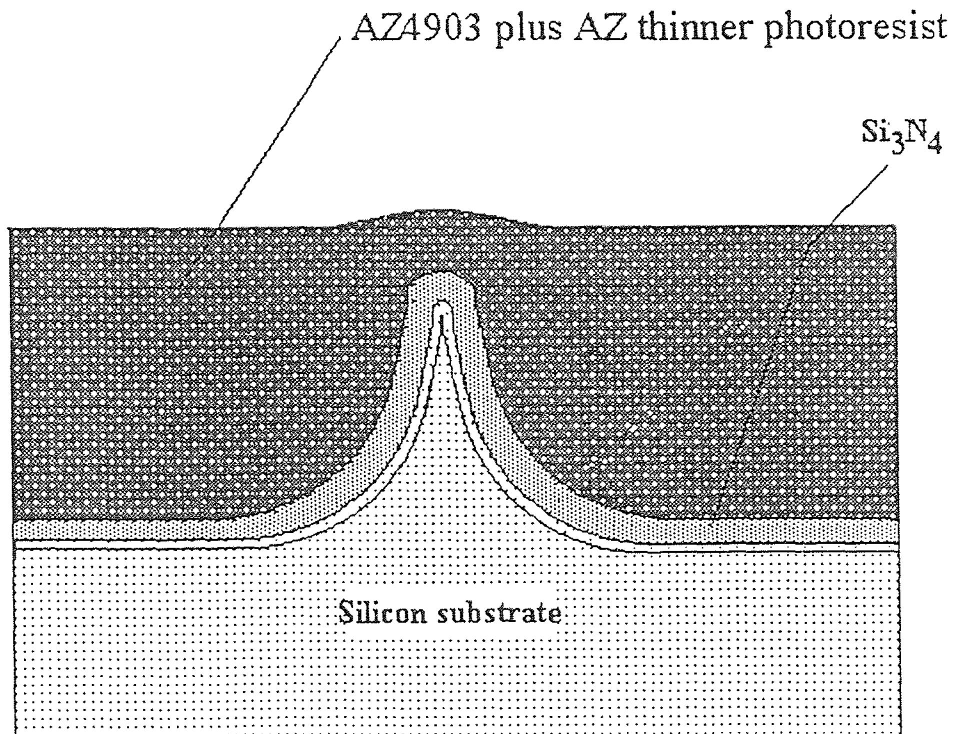


Figure 4.15 Sample with special photoresist which covers the knife edge

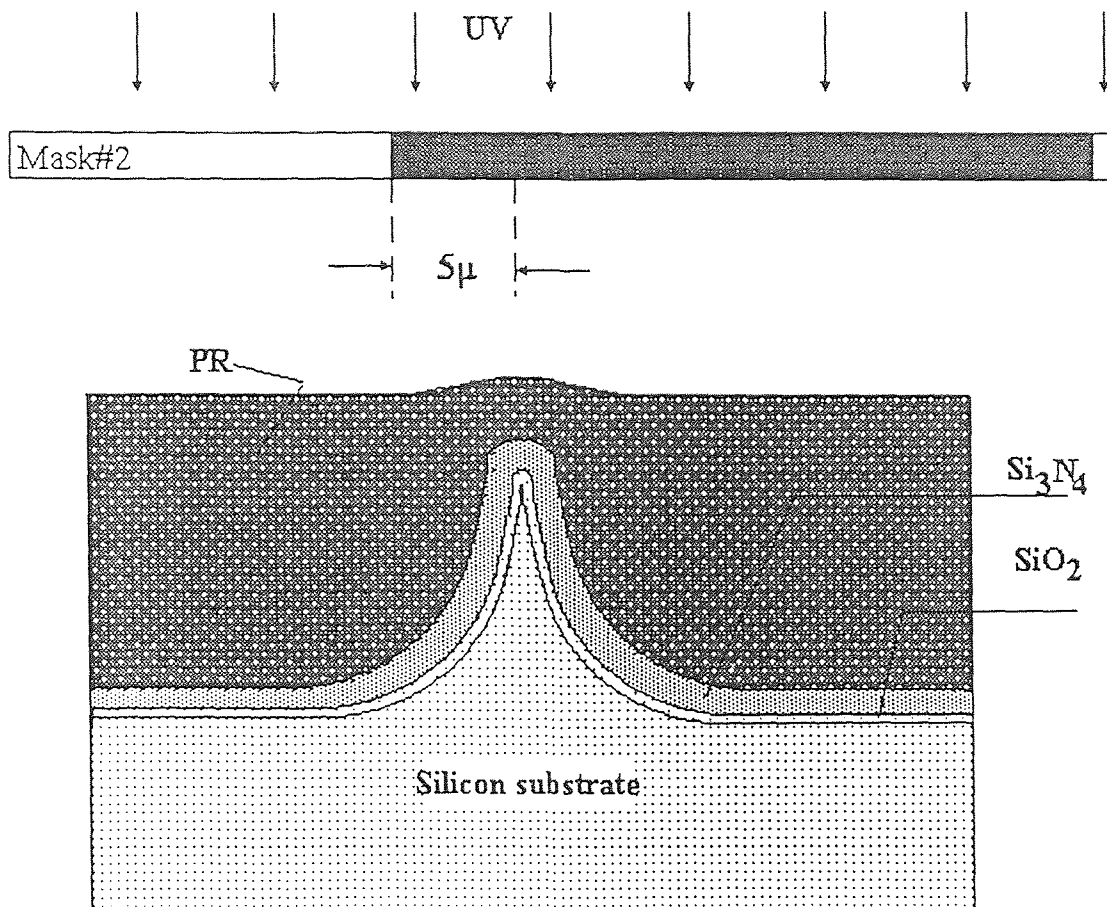


Figure 4.16 Photolithographic process using mask#2

Before the photo resist was removed, we also need to pattern the thin oxide film. Because the oxide film is only 200Å, we can not use the 7:1 BOE to etch the oxide because it etches too fast. Instead, 100:1 $HF:H_2O_2$ was used to etch the oxide. The etch rate is about 70Å/minute, so the etch time is 3 minutes. Then the photoresist is removed. After silicon nitride patterning and removal of photoresist, the sample appears as shown in Figure 4.18.

10. Anisotropic etching using chemical KOH.

KOH (potassium hydroxide) is an anisotropic silicon etchant[7] which reveals {111} surfaces. This behavior results from the fact that etch rate for {100}, {110} and {111}

planes in KOH are $R_{\{110\}} \cong 2R_{\{100\}} >> R_{\{111\}}$. Follow this fact, {110} wafers were used as our starting wafers and KOH etchant was used to vertically separate each knife. The etch solution is KOH and water. The etch rate depends on the temperature and the ratio of KOH and water. (see Appendix B)

Table 4.8 Special photolithographic process parameters for covering 5 μm high knife

Parameter	Value
Vapor HMDS temperature	135°C
Photoresist	AZ4903:AZ thinner = 3:1
Spin speed	2500 RPM
Spin time	1 minute
Resist thickness	6.7 μm
Soft bake time/Temperature	20 minutes/85°C in Oven
Exposure power density	25 mW/cm^2
Exposure time	16 seconds
Developer	AZ developer
time	15+10 seconds
Hard bake time/Temperature	20 minutes/85°C in Oven

Table 4.9 Silicon nitride plasma etching parameters

Parameter	**Value**
SF_6 flow	50 sccm
Pressure	150 mTorr
Power	400 Watts
Temperature	25°C
Etch rate	388 Å/minute

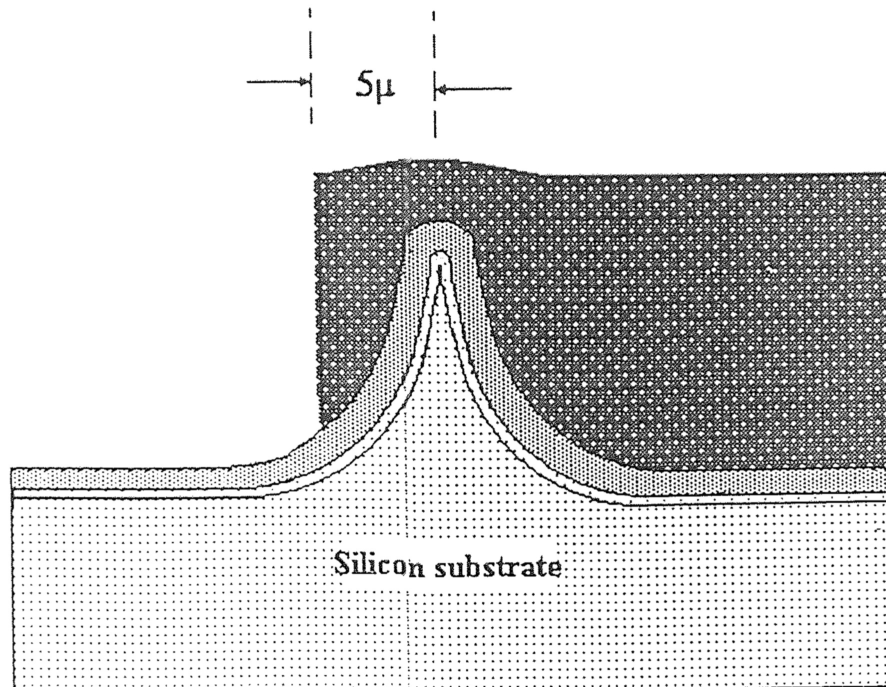


Figure 4.17 Sample after developing photoresist

Table 4.10 KOH anisotropic etching parameters

Parameter	Value
Etchant	45 w% KOH
Temperature	80°C
(110) Si μm/h	87 μm/h
(111)Si μm/h	0.05 μm/h
Time (h)	3.5 hours
Etching silicon thickness	~ 300 μm

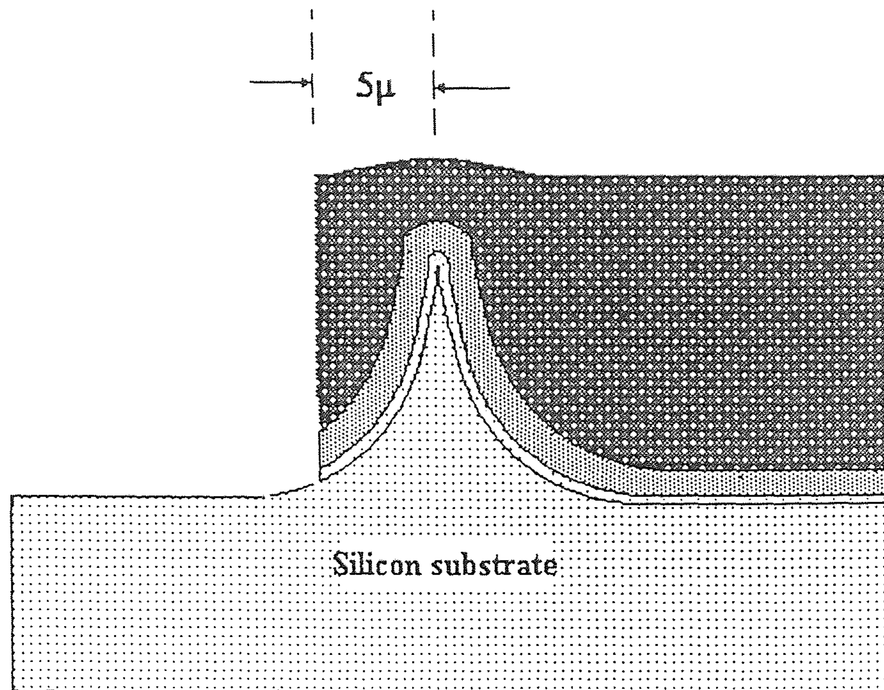


Figure 4.18 Sample after patterning silicon nitride and oxide

In our research we used 45 weight percent KOH at a temperature 80°C to etch the silicon with a silicon nitride mask, because KOH etches the silicon nitride very slowly. After 3.5 hours in KOH, the side wall of the silicon is very straight shown in Figure 4.21. Because the KOH slowly etches the {111} silicon, after 3.5 hour etching, we have about 2 μm undercutting shown in Figure 4.22 and 4.19. The KOH etching parameters are shown in Table 4.10.

11. Strip silicon nitride and oxide.

The H_3PO_4 etchant is used for striping the silicon nitride at a temperature 170°C. The etch rate is about 87Å per minute, and 23 minutes are needed to etch 2000Å silicon nitride. Then 100:1 H_2O_2:HF is used to strip the oxide in 4 minutes. The sample after striping the silicon nitride and oxide is illustrated in Figure 4.20. Silicon nitride striping

parameters are shown in Table 11. Then we can easily separate each silicon knife by breaking the whole wafer. A separated knife is illustrated in Figure 4.23.

Table 4.11 Silicon nitride striping parameters

Parameter	Value
H_3PO_4	
Temperature	170°C
Etching rate	87Å/minutes
Etching time	23 minutes

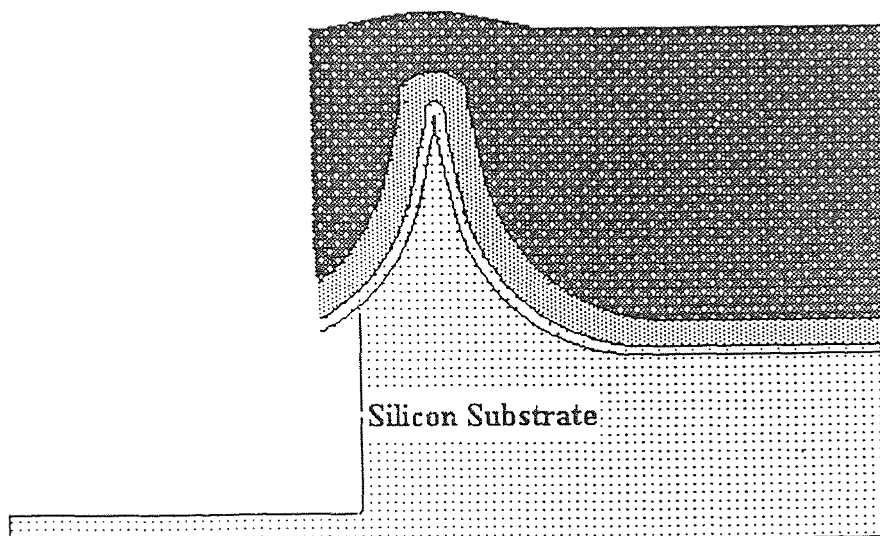


Figure 4.19 Sample after KOH etching

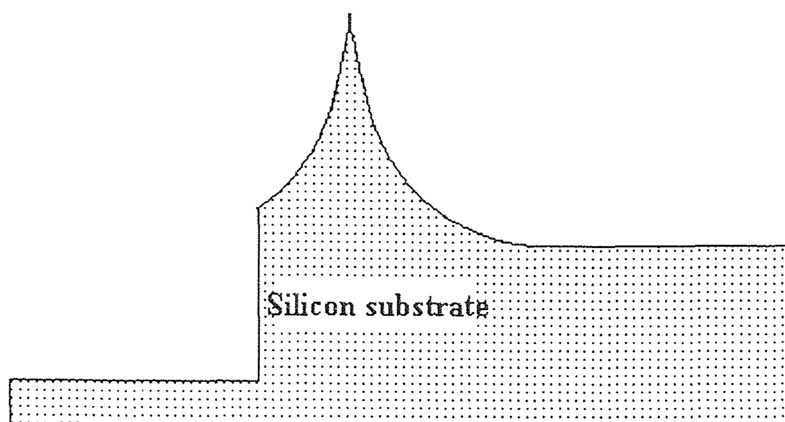


Figure 4.20 Sample after striping the silicon nitride and oxide

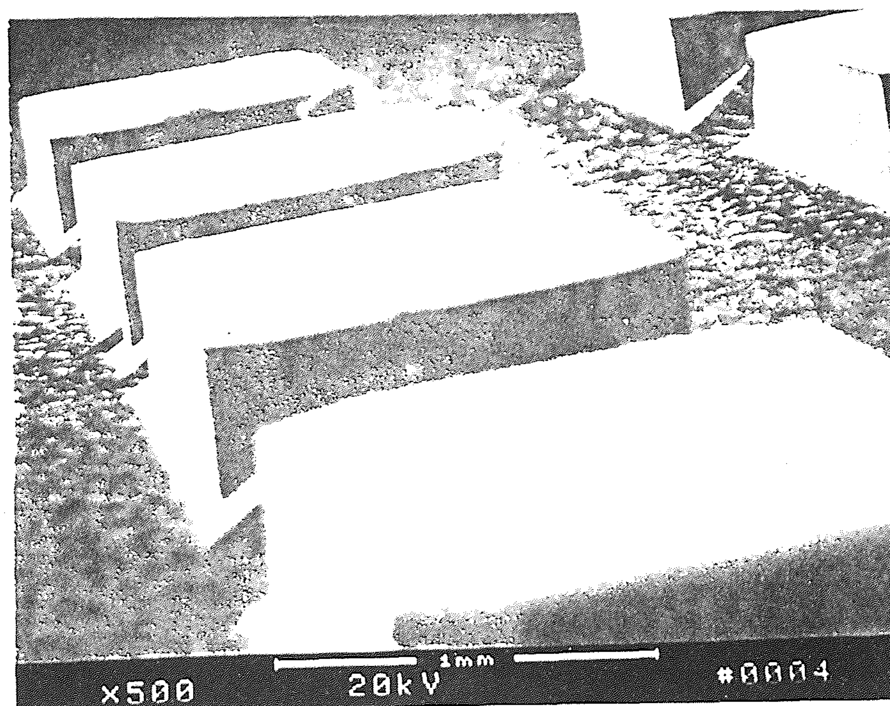


Figure 4.21 SEM photo after 3.5 hour KOH Etching
500X

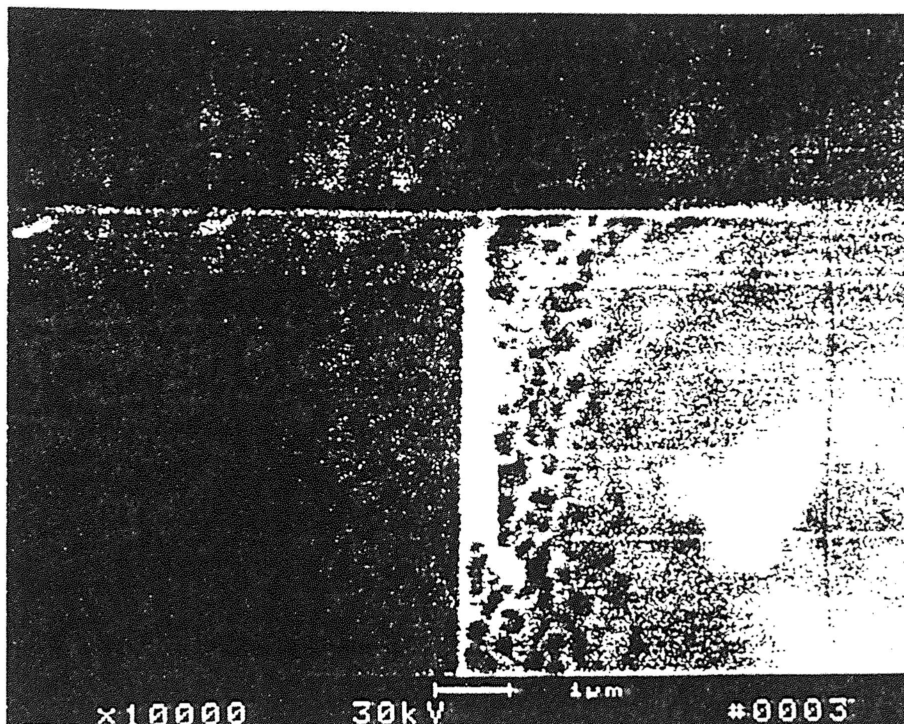


Figure 4.22 SEM photo showing undercutting after KOH etching

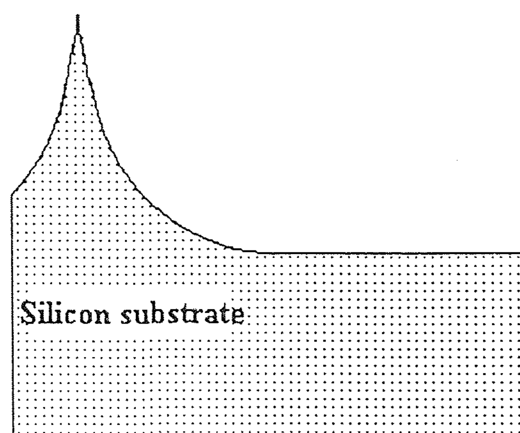


Figure 4.23 Cross-section of single knife

CHAPTER 5

CUTTING TEST OF THE ULTRASHARP SILICON KNIFE

In this chapter we will describe a simple method of testing the cutting ability of the ultrasharp silicon knife. The cutting testing was performed in an Amray 1610 scanning electron microscope (SEM).

5.1 Cutting in General

First we assume the knife is very hard, and consider only the material which is being cut:

When cutting something, we apply force F to the knife in order to force the knife to go into the material. At the point where the knife contacts the surface over an area, the pressure is F/area. If we assume that the contact area is approximate equal to 2**r** times the knife edge length, then the pressure P = k/**r**. The smaller the radius **r**, the bigger the pressure applied to the material, and the easier it is to cut the material.

Now consider the effect on the knife material. When we apply pressure larger than the threshold stress σ_{ck} for initiating compressive failure of the knife,. the knife edge cannot sustain the larger pressure, and the knife breaks. Here the σ_{ck} is related to the knife material. The harder the yield point of the material, the bigger is the value of σ_{ck}.

From the above discussion, we know we used a knife which must be both sharp and hard. Knives are usually made of diamond and steel. In this research, our target is to use silicon to make an ultrasharpen knife and to use this knife to cut biological tissue samples. We successfully made a silicon knife edge as described in chapter 4. Now we need to test the strength of silicon knife and the ability of the ultrasharpen silicon knife to cut the biological tissue.

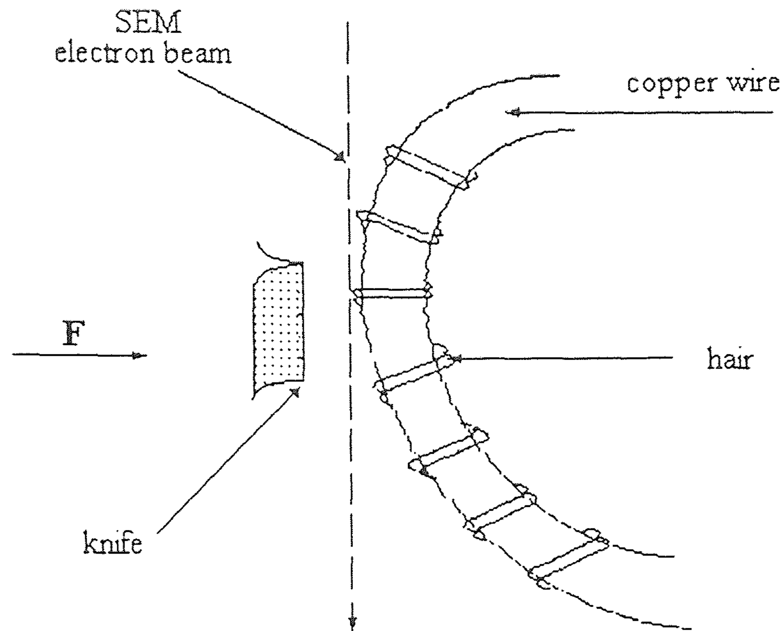


Figure 5.1 Cutting experiment

5.2 Cutting Test Experiments

In this experiment, we used human hair as the sample to be cut. The hair was wrapped on a copper wire as shown in Figure 6.1. First we must deposit a very thin metal coating on the hair surface because the hair is an insulator and when we put it in the SEM at high voltage it will get charge up and destroy the image. Then we mount the copper wire on which the hair was wrapped on an XYZ stage in the SEM chamber, and the knife is mounted on another X'Y'Z' stage. Then both stages are adjusted to bring both the hair and the knife to the same focal plane.

The first experiment was performed with an atomically sharp knife (**r** = 5Å) made with the method described in chapter 4; that is, the knife surface was uncoated atomical-sharp silicon. After the cutting test, the knife became broken as shown in Figure 5.2. This result showed that the knife was too sharp (**r** was too small) and the applied pressure

was larger than the silicon threshold stress. In order to solve this problem, we made two changes: one was to increase the radius and the other was to put some hard material over the silicon to increase the knife hardness.

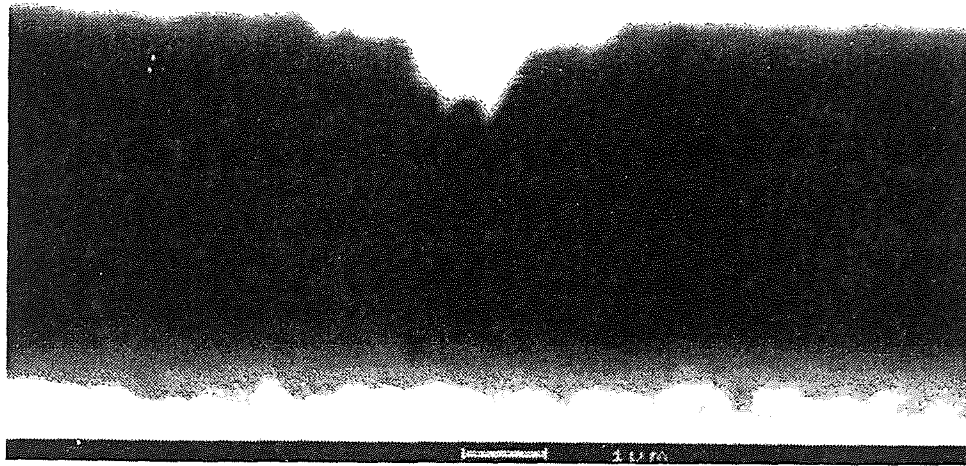
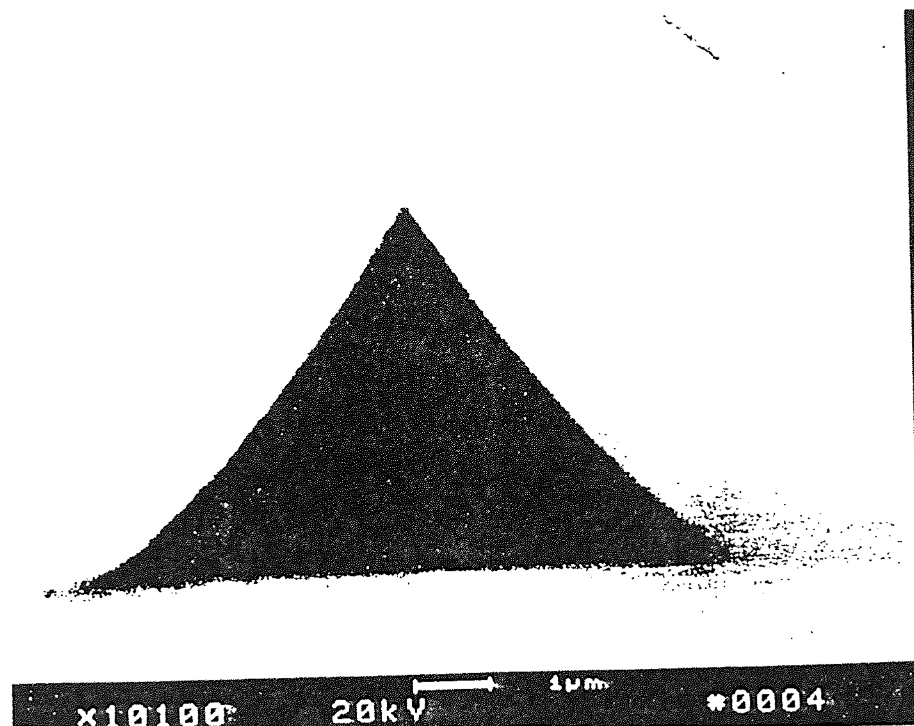


Figure 5.2 The broken silicon knife edge which didn't cover anything

The first thing we did was to blunt the knife edge to increase the tip radius **r**. We put the knife wafer in a steam oxidation furnace for 5 minutes steam oxidation at temperature 1100°C, then using 7:1 BOE to remove the oxide. This treatment is expected to increase the radius to ~ 50Å. Before and after blunt knife edge is shown in Figure 5.3a and 5.3b. Then we used dry oxidation to grow 100Å oxide at temperature 950°C, then used LPCVD at 775°C to deposit 120Å silicon nitride film. The silicon nitride film is a hard material with no microcracks, and was expected to increase the silicon knife strength.

Then cutting test experiment was repeated. The result was very satisfactory as shown in Figure 5.4a and 5.4b. The knife didn't break, and four smoothcuts were made.



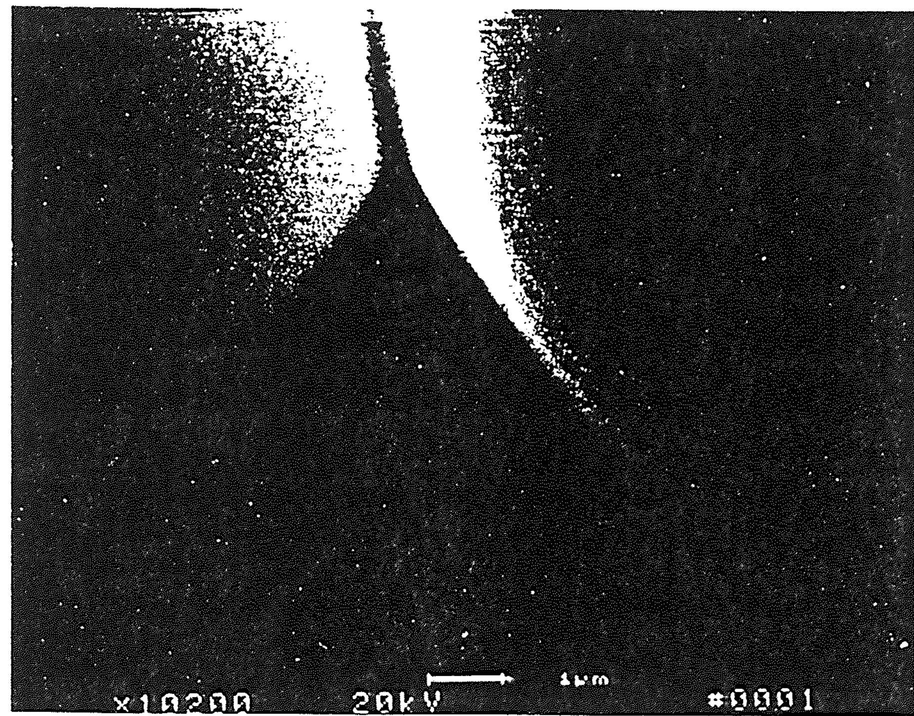
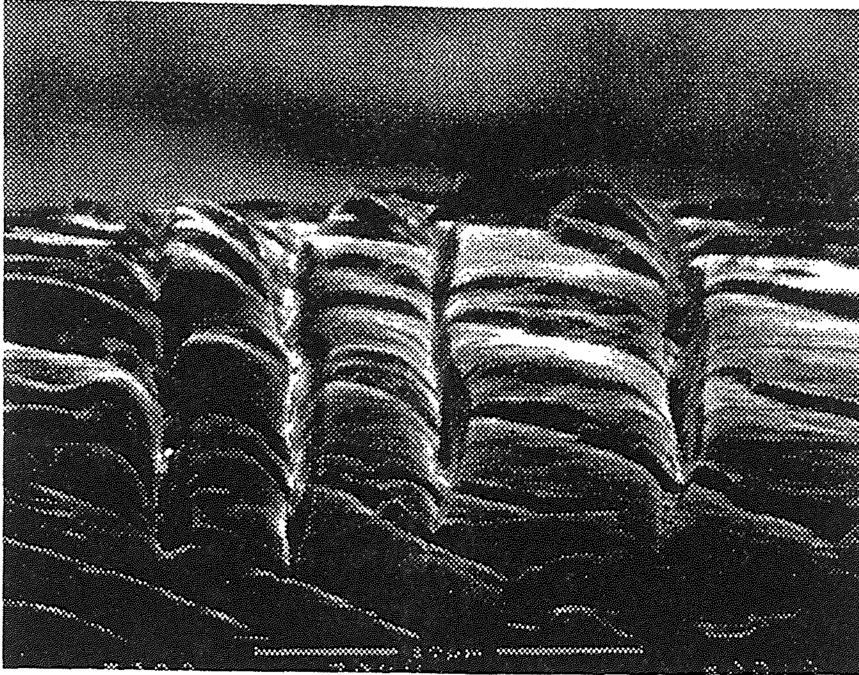


Figure 5.3 (a) Before the knife was blunt. (b) After the knife was blunt



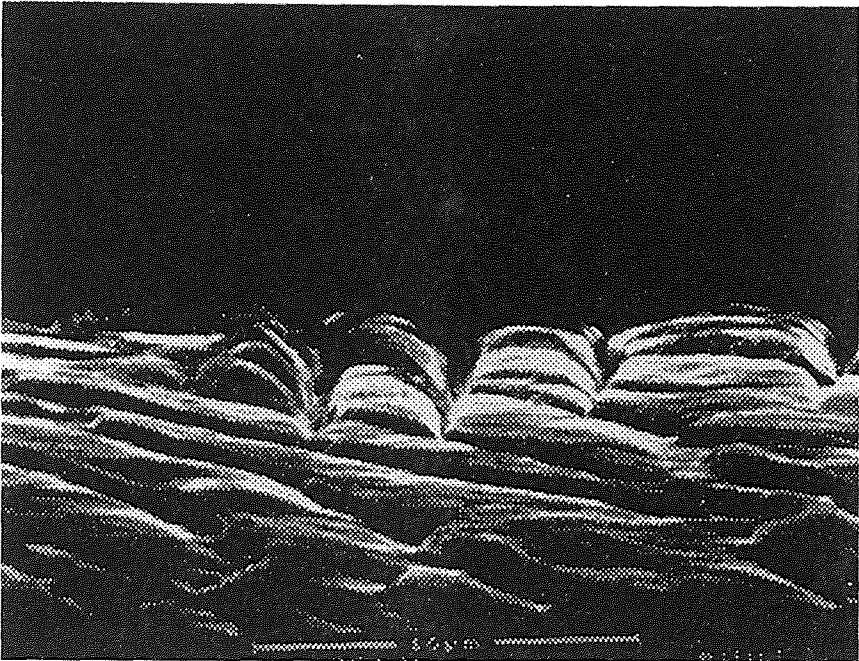


Figure 5.4 Two views at 5000X of 4 cuts made more then 1.5μm deep into the outer surface of the human hair.

CHAPTER 6

SUMMARY AND CONCLUSION

In this thesis, we demonstrated a procedure for making ultrasharp knife edges of silicon. The main results of this research are summarized:

6.1 Develop a Procedure for Making an Ultrasharp Knife

We have demonstrated a process for using silicon wafers, two photo masks and a series of semiconductor device processing steps for making an ultrasharp knife. These steps include KOH anisotropic etch, mix acids isotropic and plasma dry etch, photolithography, LPCVD silicon nitride, and thermal oxidation. This edge of the silicon blade has a radius of curvature of less then 5 nm (estimated) with a blade angle of 1~5°. This silicon knife is more than 100 times sharper than stainless steel knives currently commercially available, and the surface of the silicon knife blade is very smooth. So using this very smooth surface silicon knife to cut materials which are softer than silicon such as biological tissue and polymers is expected to result in cleaner, smoother surfaces.

6.2 Can Improve Silicon Knife Strength

From cutting test results we have shown that the silicon knife strength can be improved by (1) using a few minutes steam oxidation to blunt the silicon knife edge to increase to radius of curvature and decrease the pressure on the knife tip, and (2) coating the silicon with a thin hard material such as Si_3N_4, to increase the hardness of silicon knife.

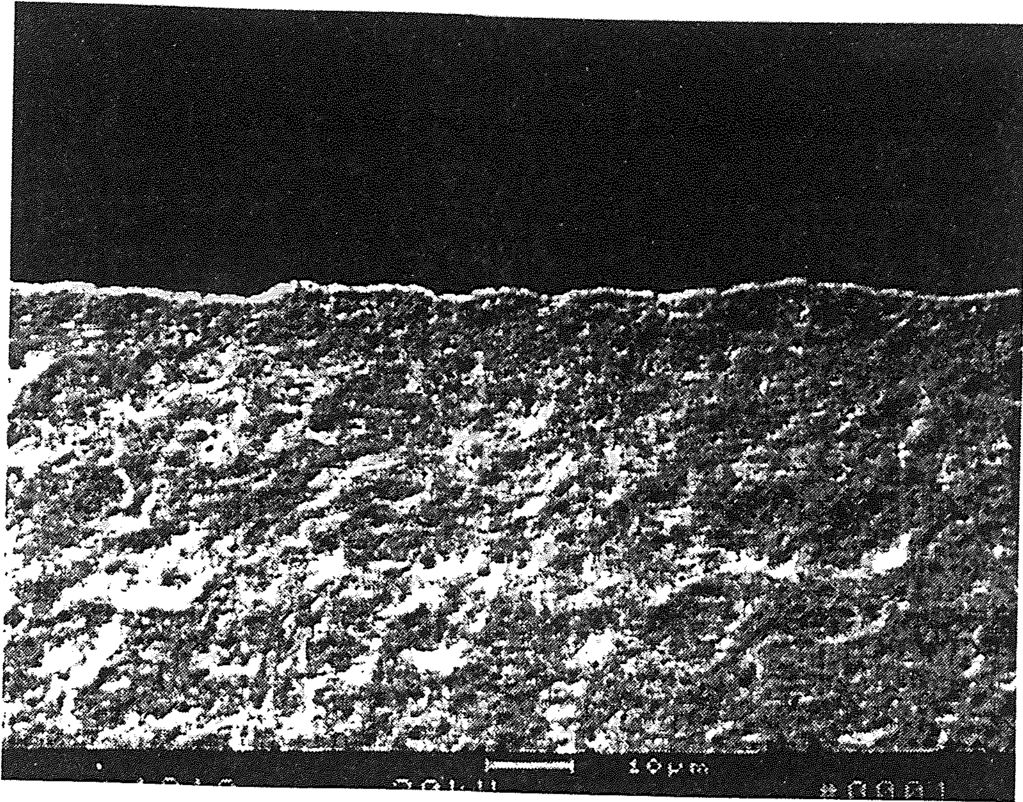


Figure 6.1 SEM photo of commercial steel microsurgical scalpel blade.
34,000X

APPENDIX A

TRAVELER
(Detailed Set of Processing Steps for Using in NJIT_MRC)

1. P-clean: 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

2. Furnace pre-clean: 100:1 H_2O:HF , Time: 1 minutes, Rinse COLD DI 10 minutes, spin dry.

3. Steam Oxidation: O_2: 7.5 SLM, Bubbler: 530 sccm, Temperature: 1050^oC , Time: 95~100 minutes.(target: 4500A), Measure: Mean and Std.Dev.

4. Photolithography: Apply Photoresist(Shipley 1813)-- Spin time: 20 second, Spin speed: 4500RPM, Oven bake: 115^oC , 20 minutes. Align and expose(Mask #1)-- expose time:10 seconds. Develop (MF319)-- 30+15 seconds, Oven bake: 115^oC , 20 minutes. Inspect.

5. Wet etch Oxide: 7:1 BOE , 25^oC ,4~5 minutes(to completion plus 10% overetch), Rinse COLD DI 10 minutes, spin dry, Inspect and Measure.

6. Reactive Ion Etch Si(Anisotropic etch Si):DRIE-100, process#3, 50 sccm SF_6, 50 sccm Freon 115, Pressure:150 mTorr, Power: 400 Watts, 25^oC, 1 minute 30 seconds, Inspect.

7. P-strip photoresist(PR): 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry, Inspect&Measure.

8. Wet etch Si: HNO_3(95%) : HF(2%) : CH_3COOH(3%) mixed acid, Temperature: 25^oC, Time: ~20 minutes, Inspect(Etched to completion?), Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

9. Remove Oxide: 7:1 BOE , 25^oC ,4~5 minutes(to completion plus 10% overetch), Rinse COLD DI 10 minutes, spin dry, Inspect and Measure.

10. P-clean: 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

11. Furnace pre-clean: 100:1 H_2O:HF, Time: 1 minutes, Rinse COLD DI 10 minutes, spin dry.

12. Dry Oxidation: O_2: 7.5 SLM, Temperature: 950^oC , Time: 12~18 hours, Measure: Mean and Std.Dev. Inspect (the knife edge is sharpen?)

13. Remove Oxide: 7:1 BOE , 25^oC ,~2 minutes (to completion plus 10% overetch), Rinse COLD DI 10 minutes, spin dry, Inspect and Measure.

14. Repeat step 10 to 13 several times until the knife edge is sharpen.

15. P-clean: 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

16. Furnace pre-clean: 100:1 H_2O:HF, Time: 1 minutes, Rinse COLD DI 10 minutes, spin dry.

17. Dry Oxidation: O_2: 7.5 SLM, Temperature: 950^oC , Time: 20 minutes , Measure: Mean and Std.Dev(target 200A).

18. P-clean: 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

19. Furnace pre-clean: 100:1 H_2O:HF, Time: 1 minutes, Rinse COLD DI 10 minutes, spin dry.

20. Deposit LPCVD Si_3N_4: DSC: 50sccm, NH_3: 120 sccm, Pressure: 400 mTorr, Temp: 775^oC , 40 minutes, Measure(target 2000 A).

21. Photolithography: Apply Photoresist(Shipley 1813)-- Spin time: 20 second, Spin speed: 4500RPM, Oven bake: 115^oC , 20 minutes. Align and expose(Mask #2)-- expose time: 10 seconds. Develop (MF319)-- 30+15 seconds, Oven bake: 115^oC, 20 minutes. Inspect.

22. Pattern Si_3N_4: DRIE-100, process#2, 50 sccm SF_6, Pressure:150 mTorr, Power: 400 Watts, 25^oC, 5 minute, Inspect.

23. Etch oxide: 100:1 H_2O:HF , Time: 4 minutes, Rinse COLD DI 10 minutes, spin dry.

24. P-strip photoresist(PR): 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry, Inspect&Measure.

25. Anisotropic etch Si: KOH 45%(w), Temp: 80^oC , Time: 3 hours, Inspect. Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

26. P-clean: 5:1 H_2SO_4:H_2O_2 , Temperature: 110^oC , Time: 10 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

27. Strip Si_3N_4: H_3PO_4, Temp: 170^oC , Time: 30 minutes, Rinse HOT DI 10 minutes, Rinse COLD DI 5 minutes, spin dry.

28. Oxide strip: 100:1 H_2O:HF , Time: 4 minutes, Rinse COLD DI 10 minutes, spin dry.

APPENDIX B

ETCH RATE AND RATIOS OF KOH ETCHANT ETCH SILICON[10]

wt. pct. of KOH flakes in H_2O	true KOH wt. pct.	temp. °C	(110) Si μ/hr	(111) Si μ/hr	Ta Å/hr	Si_2O Å/hr	(110) ÷ (111)	(110) ÷ Ta	(110) ÷ Si_2O
10%	9%	23	0.49	0.13	oxide	5.3	3.8	∞	920
10%	9%	40	4.6	0.49		37	9.4		1200
10%	9%	50	19	0.85	oxide	99	22	∞	1900
10%	9%80	80	100	3.1	oxide	1100	32	∞	910
20%	18%	23	3.3	0.10	oxide	7.5	33	∞	4400
20%	18%	40	13	0.32		60	47		2800
20%	18%	50	21	0.53	oxide	120	40	∞	1800
20%	18%	80	130	1.2	1000	1500	110	1300	870
25%	22.5	23	3.0	0.087	oxide	8.6	34	∞	3500
25%	22.5	40	13	0.23		60	57		2200
25%	22.5	50	23	0.42	oxide	160	55	∞	1300
25%	22.5	60	41	0.51			80		
25%	22.5	70	69						
25%	22.5	80	130	1.2	4000	1600	110	320	810
25%	22.5	100	360	303			110		
30%	27%	23	2.8	0.070	90	9.7	40	310	2900
30%	27%	40	10	0.24	400	48	42	250	2100
30%	27%	50	24	0.29	1000	180	83	240	1300
30%	27%	80	130	0.93	10000	1900	140	130	680
40%	36%	23	2.3	0.031	300	9.9	74	77	2300
40%	36%	40	9.0	0.094	700	51	96	130	1800
40%	36%	50	22	0.15	2500	130	150	88	1700
40%	36%	80	120	0.69	9000	2100	170	130	570
50%	45%	23	1.2	0.007	400	11	160	30	1100
50%	45%	40	4.4	0.026	2000	55	170	22	800
50%	45%	50	10	0.062	4000	180	160	25	560

50%	45%	80	87	0.48	20000	1900	180	44	460
60%	54%	40	1.7	0.006	1000	24	200	17	710
60%	54%	50	4.2	0.024	2000	81	180	21	520
60%	54%	80	34	0.41	10000	1900	83	34	180

REFERENCE

[1] R. B. Marcus, T. S. Ravi, T. Gmitter, K.Chin, D.Lin, W. J. Orivs, D.R. Ciarlo, C. E. Hunt and J. Trujillo, "Formation of Silicon Tips with < 1 nm Radius", *Applied Physics Letters*, **56**(3), 236(1990)

[2] R. B. Marcus and T. T. Sheng, "The Oxidation of Shaped Silicon Surfaces" *Journal of the Electrochemical Soiciety*, **129**(6), 1278(1983)

[3] Y. Sakina, T. Ohno and S. Matsumoto, "Two-Dimensional Analysis of Thermal Oxidation of Silicon", *Japanese Journal of Applied Physics*, **22,** L514(1983)

[4] T. S. Ravi, R. B. Marcus and D.Liu, "Oxidation Sharpening of Silicon Tips", *Journal of the Vacuum Science Technology*, **B9**(6), Nov/Dec, 2733(1991)

[5] E. C. Clayden, "Histroy of Microtomes", *Practical Section Cutting and Staining*, 21(1971)

[6] Norma Reid, "Ultramicrotomy", *Practical Methods in Electron Microscopy*, Chap 3, **3**, 246 (1974)

[7] K. E. Bean, "Anisotropic Etching of Silicon", *IEEE Transactions of Electron Devices*, **ED-25**(10), 1185(1978)

[8] B.E. Deal and A. S. Grove, "General relationship for the Thermal Oxidation of Silicon", *Journal of the Applied Physics*, **36**(12), Dec,3770(1965)

[9] S.M.SZE, "Semiconductor devices Physics and Technology". *AT&T Bell Laboratories, Murray Hill,NJ*

[10] L.D.Clark and D.J.Edell, "KOH:H_2O Etching of (110) Si, (111) Si, SiO_2 and Ta: an Experimental Study" *Proceeding, IEEE, Conference*, 1987