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**FABRICATION OF SILICON FIELD EMISSION TIPS
FOR VACUUM MICROELECTRONICS
BY KOH/ ALCOHOL/ WATER ETCHING**

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ABSTRACT

The fabrication of sharp silicon tips for field emission cathodes by KOH/Alcohol/Water (KAW) solution was investigated. The KOH/Alcohol/Water solution was found to work better and easier than the Ethylene-Diamine/Pyrocatechol/Water solution in etching silicon tips. It etched the (100) silicon surface more slowly, but in a more controllable manor. The resulting tips were usually very uniform and pretty sharp in most studies.

Actually, there were some systems showing non-uniform etching behavior. However, we were able to demonstrate that the uniformity could be improved by shifting the reaction from mass transfer controlled to chemical kinetics controlled. Such technique could allow us to fabricate uniform silicon cones even in a very primitive apparatus with non-uniform mass transfer.

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(I) INTRODUCTION

Micro silicon sharp tip fabrication has been a major concern in the development of the vacuum microelectronics technology. It is believed that making a micro scale vacuum tube will have numerous advantages. It will be much faster than the old conventional vacuum tube because of its tiny size. At the same time, it will enjoy the advantage of having high electron emission, just like the old conventional vacuum tube. In addition, the micro vacuum tube will have the advantages of radiation-hardness and thermal insensitivity over the conventional integrated circuits. In order to make a good field emission point, we need a very sharp tip in the vicinity of a big flat anode. The sharper the tip is, the better and easier the electron field emission will be. Thus the fabrication of a sharp point cathode is one of the major key steps in the development of vacuum microelectronics.

(II) BACKGROUND INFORMATION

In terms of production and quality control, besides good sharp tips, we also need uniformity over the whole wafer. Thus the experiments were actually divided into 2 main categories :

1. to study how to fabricate the silicon tips with various compositions of the KOH/Alcohol/Water (KAW) etching solution^{1,2,3,4,5}; and
2. to understand how to control the uniformity of the silicon tips etched by the KOH/Alcohol/water solution.

(1) Silicon Etching with KOH/Alcohol/Water (KAW)

The etching of silicon in KAW mixtures is a heterogeneous reaction. The main phases are a liquid layer of aqueous KOH solution with small

amount of alcohol (layer 1) and a liquid layer of alcohol with a small amount of aqueous KOH solution (layer 2). Layer 2 is the main etching phase; whereas layer 1 the main excess source of the alcohol to layer 2. Without layer 1 on top of the layer 2, any alcohol dissolved in the layer 2 may be lost by evaporation very fast.

The possible stoichiometric equation for the KAW-silicon reaction is :

which is very similar to the one without alcohol. The alcohol here seems to affect the mass transfer and the kinetics on the reaction surface. The resulting catalytic effects are changing the anisotropy and slowing down the etching rates.

Without the alcohol, the etching rates for the three major crystallographic faces are in the order of (110)>(100)>(111). With the alcohol, the new order becomes (100)>(110)>(111). For example, for a 36% KOH solution without alcohol at 80°C, the etching rates for (100) (110) and (111) are 0.96 micron/min, 1.63 micron/min and 0.17 micron/min. However, with isopropyl alcohol, the etching rate is increased to 1.06 micron/min for (100) (+10%), but is decreased to 0.60 micron/min for (110) (-63%) and 0.06 micron/minute for (111) (-65%). The ratio of the etching rates for (110):(100) changes from 1.7:1 to 0.57:1 .

This big change in the (110):(100) etching ratio will certainly affect the formation of the cone. On a (100) silicon wafer, etching at (110) means etching sideways, whereas etching at (100) means etching downward. A higher (110):(100) etching ratio will etch sideways faster to form a blunt tip. In contrast, a lower ratio will etch downward faster to make a sharper tip. Therefore, by adding the alcohol to change the ratio from >1 to <1, we can fabricate sharper and better tips.

(2) Controlling Etching Uniformity

In here, we are talking about the uniformity over the whole wafer. Generally, uniform etching means the reaction rate is the same on the whole wafer. The chemical reaction rate will depends on both the chemical kinetics and the mass transfer. It may be totally chemical kinetics controlled, totally mass transferred controlled, or just in between.

Chemical kinetics is referred to the maximum possible rate of a chemical reaction under a specific experimental environment; whereas the mass transfer is referred to the rates of the reagents coming to the surface and the products leaving it. If the maximum possible reaction rate is much faster than the mass transfer, the actual reaction rate will be limited/controlled by the mass transfer. On the other hand, if the maximum possible reaction rate is much slower than the mass transfer, the actual reaction rate will be just as fast as the maximum possible rate. In this case, the actual reaction rate will be independent of the mass transfer, or chemical kinetics controlled.

There are 2 ways to obtain uniform etching. First, if the etching reaction is chemical kinetics controlled, we will have uniform etching rate over the whole wafer. On the other hand, if the reaction is mass transfer controlled, then we will need a etching system that will provide uniform mass transfer.

However, the preliminary setup in our etching system could only enhance mass transfer, but would not be able to provide uniform mass transfer across the whole wafer. Thus, if we had a mass transfer controlled reaction, we would see non-uniform etching. In such case, we had to either design a very sophisticated mass transfer etching cell, or shift the reaction from mass transfer controlled to kinetics controlled.

(II) EXPERIMENTS

(1) Fabrication of Silicon Tips with KAW Solutions

Tips were fabricated by etching (100) silicon wafer surfaces with solutions made of 6 parts KOH solution, 1 part alcohols and surfactant. The KOH solution is a 36% (wt.%) solution in water. Three types of alcohol had been tried in our experiments. They included isopropyl alcohol, n-butyl alcohol and sec-butyl alcohol. The surfactant is the Triton^R X-100. Usually, it was about 0.3-0.4 % by volume. These solutions would etch silicon anisotropically.

The wafers used for the etching study were mainly (100) wafers. Since etching behavior varies with the dopant in the wafer, both N-type and P-type wafers were used in the study.

The mask used in this studies consisted of 10 microns squares of silicon nitride as the etching caps. We had tried with 5-micron etching caps , however they did not provide enough etching protection to accomplish the task. These caps were in the matrix of 20 microns apart.

The experimental setup was made up with regular chemical laboratory apparatus. Figure (1) shows a sketch of the etching setup. The etching bath was a 1000 ml beaker inside a (190 X 100 ml) crystallizing beaker, which was sitting on a electromagnetic stirring heating plate. The wafer was put in the solution with a single wafer holder. The whole solution was mixed continously with a magnetic stirring bar. Most of the experiments were done at 57°C, except only a few at 51-52°C for the uniformity study.

(2) Controlling the Uniformity

One of the biggest challenges in etching silicon wafers chemically is the control of the uniformity over the whole wafer surface. In these uniformity

Figure (1) - The Apparatus for the Etching Bath

control experiments, we were trying to improve the uniformity by manipulating the chemical kinetics verse the mass transfer.

We picked a KAW etching system that produced non-uniform tips due to mass transfer problem. The system chosen was a KOH/Isopropyl-Alcohol/Water solution at 57°C for a p-type wafer. Usually, such etching system would produced non-uniform cones after a 40-minute etching time.

In our plan, we did not want to spend a lot of time and money to develop a sophisticated mass transfer reactor to achieve uniform mass transfer and thus uniform etching. Thus, we took the other option - i.e. to shift the reaction from mass transfer controlled to chemical kinetics controlled. This could be done simply by slowing down the etching rate but keeping the mass transfer relatively unchanged (or with only a relatively small decrease).

For this type of etching solutions, we knew that the diffusivities of the chemical reagents and products should alter only slightly with the temperature. However, the maximum possible reaction rate was very sensitive to any temperature changes. Thus, we decided to lower the temperature by a few degrees, which in turn should slow down the reaction. This should be able to shift the reaction to kinetics controlled. If not, we would lower the temperature a few more degrees until improvement in the uniformity was evident.

(III) RESULTS & DISCUSSION

(1) General Results

We found that the KOH/Alcohol/Water (KAW) solution worked much better than the old Ethylene-Diamine/Pyrocatechol/Water (EPW) solution in etching silicon tips. Generally, theses KAW solutions etched more slowly than the EPW solutions (40-50 minutes vs. 5-10 minutes). They were much

easier to control and the resulting tips were more uniform. (See Figure (2) for examples.)

We were able to fabricate cones with fairly sharp tips in a more controllable manner. Some of the wafers were cut up into halves so that we could measure the angles. Usually, the vertex angles were around 70° , whereas the base angles were around 55° .

In general, the cones seemed to have multiple faces (from 8 to 16 faces). They looked like either octagonal cones or round square cones. (See Figures (3) and (4) for examples.)

In Table (1), we have summarized the results of these etching studies. These should be very good guidelines for our future work.

(2) Uniformity Improvement

As we have described earlier, the apparatus for our wafer etching system was very primitive. It was very difficult to obtain uniform mass transfer over the whole wafer. In the case of mass transfer limited reactions, we would have non-uniform etching.

One of the ways to improve the etching uniformity in such primitive apparatus was by shifting the reaction from mass transfer controlled to chemical kinetics controlled. This could be done by just lowering the temperature by a few degrees, because the chemical kinetics in the KOH/Alcohol/Water system was more sensitive than the mass transfer. In other words, the chemical kinetics would be slowed down relatively much more than the mass transfer.

The system chosen for demonstrating this uniformity improvement technique was a KOH/Isopropyl-Alcohol/Water solution at 57°C for a p-type wafer. After 40 minutes of etching time, the wafer showed non-uniform etched cones. (See Figures (5-a) and (5-b).) As we can see, some of the

(a) 70° Side View of Cones Etched by
KOH/2-Propanol/Water Solution
at 57°C.

(b) Top View of Cones Etched by
KOH/1-Butanol/Water Solution
at 57°C.

Figure (2) - Examples of the Uniform Cones Etched by KOH/Alcohol/Water Solutions.

(a) 70° Side View of Cones Etched by
KOH/2-Butanol/Water Solution
at 57°C. The Square "Hats" are
the 10 micron X 10 micron
SiN Etching Caps.

(b) Top View of Cones Etched by
KOH/2-Butanol/Water Solution
at 57°C.

Figure (3) - Examples of the Octagonal Cones Etched by KOH/Alcohol/Water Solution.

(a) 70° Side View of Cones Etched by
KOH/2-Propanol/Water Solution
at 57°C.

(b) Top View of Cones Etched by
KOH/2-Propanol/Water Solution
at 57°C.

Figure (4) - Examples of the Round Square Cones Etched by KOH/Alcohol/Water Solution.

<u>Alcohol</u>	<u>Temperature</u>	<u>Wafer Type</u>	<u>Time Required</u>	<u>Uniformity</u>	<u><100> Base Surface</u>	<u>Cone Shape</u>
isopropyl	57°C	N-type	50 min	good	smooth	round square
isopropyl	57°C	P-type	40 min	bad	smooth	octagonal
isopropyl	51-52°C	P-type	79 min	good	slightly rough	round square
n-butyl	57°C	N-type	45 min	good	smooth	round square
n-butyl	57°C	P-type	50 min	good	rough	octagonal
sec-butyl	57°C	N-type	40 min	good	smooth	octagonal
sec-butyl	57°C	P-type	40,47 min	good	smooth	octagonal

Table (1) - Results of Etching <100> Silicon Wafers with KOH/Alcohol/Water Solutions.

(a) 70° Side View

(b) Top View

Figure (5) - A P-Type Silicon Wafer Etched with KOH/Isopropyl-Alcohol/Water at 57°C for 40 minutes.

cones were etched completely while the others were under etched. Apparently, the required etching time should be 40 minutes and the non-uniformity was caused by non-uniform mass transfer.

We repeated the above experiment, not at 57°C, but at 51°C. As expected, the the etching rate was slowed down. After 40 minutes of etching time, all the cones were not completed, but they were in similar shapes. (See Figure (6-a) and (6-b).) It took a total of 79 minutes, versus 40 minutes, to complete the etching. (See Figure (7-a) and (7-b).) So the kinetic rate was nearly half cut.

As shown in Figure (7-a) and (7-b), the resulting etching cones were much more uniform than those etched at 57°C. So, this experiment did demonstrated that we could improve the etching uniformity by shifting the reaction into chemical kinetics controlled mode.

(VI) SUMMARY

The KOH/Alcohol/Water (KAW) solution worked much better and easier than the Ethylene-Diamine/Pyrocatechol/Water (EPW) solution in etching silicon tips. Generally, the KAW solutions etched the silicon surface more slowly , but in a more controllable manor. The resulting tips were usually pretty sharp and uniform in most of our studies.

In addition, we had demonstrated that we could improve the etching uniformity by shifting the reaction from mass transfer controlled to chemical kinetics controlled. The special technique could allow us to fabricate uniform cones even in a very primitive apparatus with non-uniform mass transfer.

(a) 70° Side View

(b) Top View

Figure (6) - A P-Type Silicon Wafer Etched with KOH/Isopropyl-Alcohol/Water at 51°C for 40 minutes.

(a) 70° Side View

(b) Top View

Figure (7) - A P-Type Silicon Wafer Etched with KOH/Isopropyl-Alcohol/Water at 51°C for 79 minutes.

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