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Fabrication of high aspect ratio silicon micro-tips for field emission devices

IN JAE CHUNG, D. B. MURFETT, A. HARIZ, M. R. HASKARD
Microelectronics Centre, Department of Electronic Engineering, University of South Australia, The Levels, South Australia, 5095, Australia

The evolution of higher order {221} and {331} crystal planes during corner undercutting in the anisotropic etching of (100) silicon is discussed, and the occurrence of highly vertical (72.5°) {311} planes unique to KOH etches are demonstrated. Using a combined etching technique, very high aspect ratio micro-tips are formed and their distinct advantages for vacuum microelectronics and field-emission devices (FED) are described.

1. Introduction

Aided by highly developed IC technologies the field of vacuum microelectronics is once again active due to its inherent advantages including temperature insensitivity, radiation hardness, faster carrier velocity, and no carrier scattering in the medium [1, 2]. Various forms of electronic devices are now returning to the field of vacuum electronics to achieve superior performance over current technologies. One such field of current prominence is flat-panel displays. Research into the production and development of "micro-tips" for use in this and other similar vacuum devices has markedly increased in recent years.

Cold cathode type field-emitter devices (FED) emit electrons under an intensive electric field, which is governed by the Fowler–Nordheim tunnelling process [3]. Electrical performance of these field emitters is strongly dependent on both the work function of the material used, and the shape and sharpness of the emitter [3]. In line with this, various types of field emitters have been proposed including the Spindt type metal field-emitter, silicon field-emitter, and the horizontal type field-emitter [4]. Silicon field-emitters have their own advantages such as easy implementation of the drive circuit in the course of processing, easy controllability, abundance of material, and well defined and developed technologies.

Although dry etching technologies have been used extensively in the fabrication of field-emitters [5], "there is renewed interest in wet etching in situations where features are not submicrometer, dimensional control is essential, and surface damage is intolerable. Wet etching in sensitive to crystallographic orientation, enabling low work function facets to be obtained, it produces minimal subsurface damage" [6]. Proposed processes for making silicon field-emitters are classified into three categories; (1) isotropic etching of silicon using a composition of nitric acid, acetic acid (or water), and hydrofluoric acid (NWH) [7]; (2) orientation dependent chemical etching using anisotropic etchants [8]; and (3) combined etching techniques [9].

Each of the proposed processes has its own advantages and disadvantages. In the case of isotropic etching – although it results in a sharpened pyramid type emitter – there is a distinct lack of controllability. In the case of anisotropic etching, the structures have an inferior electrical performance resulting from their shape. Using combined etching techniques these problems can be overcome at the expense of an increase in the complexity of processing. The object of this paper is to demonstrate a set of etching conditions that when optimized result in the fabrication of sharp high aspect ratio micro-tips for FEDs.

Various etchants were researched in order to produce high aspect ratio micro-tips. In the course of this work we found that KOH produced structures different from those previously published. Previously described corner undercutting to fast etching {221} and {331} planes using KOH was found to occur and be dependant on the mask orientation. Furthermore, continued etching resulted in the appearance of high aspect ratio {311} planes with ideal characteristics for the basic structure of a silicon micro-tip. Using a two-step etching process with NWH as the second etchant, the tips of the basic structures were sharpened to form high quality micro-tips. A mixture of ethylenediamine–pyrocatechol–pyrazine–water (EPW) did not show the same characteristics as KOH, and apparently corner undercutting proceeds only to the {221} planes.

2. Experimental procedure

All experiments were conducted using p-type, (100) oriented, 1 Ω cm boron doped silicon wafers. The substrates were first cleaned with chromic acid at 105 °C and the native silicon dioxide was removed using a 5% HF solution. Thermal oxidation was performed at 1100 °C with water steam, to a final thickness of 0.5 μm. The silicon dioxide was patterned with a test mask and etched with 5.6% buffered HF solution, leaving silicon dioxide caps of various shapes, orientations and dimensions ranging from 6–14 μm. These silicon dioxide caps included circles, squares and 127°/143° octagons aligned to various crystal planes including the [100], [110], [210] and [310] directions to determine the resultant etch planes for each circumstance. Micro-tips were formed using a matrix of etchant types and etching conditions, and results were analysed using a scanning electron microscope (SEM).

2.1. Anisotropic etching with KOH

The patterned silicon wafers were etched using a 40% KOH solution at 80 °C in a double water bath with constant agitation. The measured etch rate of the solution is about 1.0 μm per min. Fig. 1 represents the experimental set up.

2.2. Anisotropic etching with EPW

As a comparison of etch results, anisotropic etching with ethylene-diamine, pyrocatechol, pyrazine and water (EPW) was also performed. The composition of the EPW solution used was the standard "F-etch" as described by Reisman *et al.* [10], namely E: 75 ml, p: 24 g, W: 24 ml, Pyrazine: 0.45 g. Its etch rate is about 10 μm per min at 115 °C.

2.3. Two step etching of silicon with KOH followed by NWH

This process was devised as a simple and easy manufacturing process to produce micro-tips having a high aspect ratio. First the specimens were etched with 40% KOH which was then followed with NWH up to the apex of the 14 μm pattern. The NWH solution consists of nitric acid, water and hydrofluoric acid in a 50:20:6 volumetric ratio, and its etch rate is about 3.6 μm per min at room temperature.

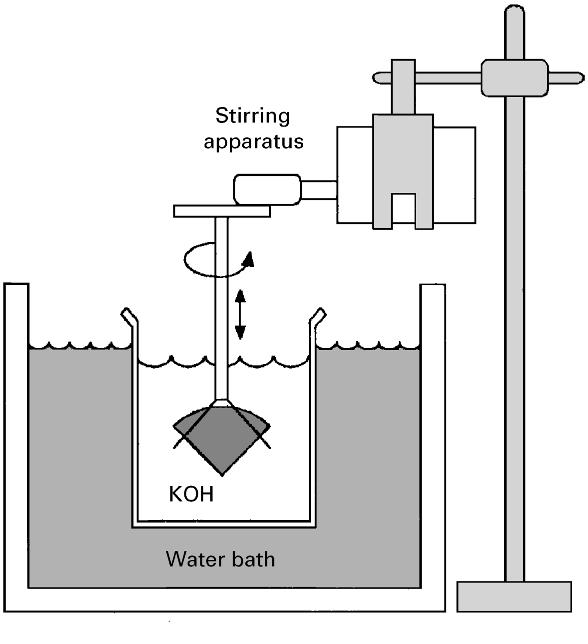


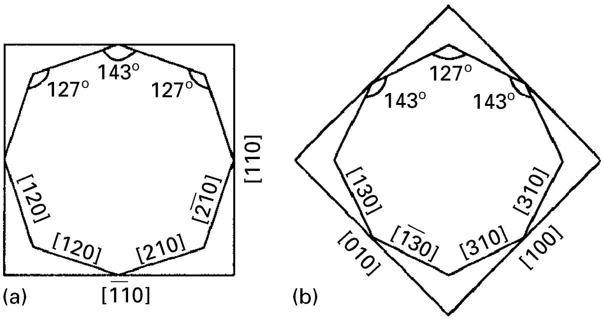
Figure 1 40% KOH etching apparatus.

3. Results and discussion

The basic nature of anisotropic etchants to etch back to {111} planes is well known, as is the occurrence of corner undercutting of convex structures. However, although various works have discussed the results of corner undercutting in anisotropic etching of (100) silicon, there is some debate as to the exact nature of the "secondary" planes to which various etchants preferentially etch. In his 1978 work [11], Bean described corner undercutting to {331} planes along the ⟨310⟩ directions and at 46.51° to the (100) surface (Fig. 2b). Wu and Ko [12] have since disputed this and stated that the planes are in fact {212} planes along the ⟨210⟩ directions and at 48.19° to the (100) surface (Fig. 2a). It can be seen that these sets of planes are very similar in appearance in both angle to the (100) surface and the octagonal pattern made at the interface, and hence determination of the correct planes requires close observation of both factors (Fig. 3).

3.1. Etching with KOH

It is apparent from the experimental procedure conducted that the selection of either {221} or {331} is generally (but not exclusively) dependant upon the orientation of the etch mask (Fig. 2a and b). Masks



(from Wu and Ko, [12])

Figure 2 Square SiO_2 masked areas undercut back to hexagonal mesas bounded by ⟨210⟩ or ⟨310⟩ crystal planes.

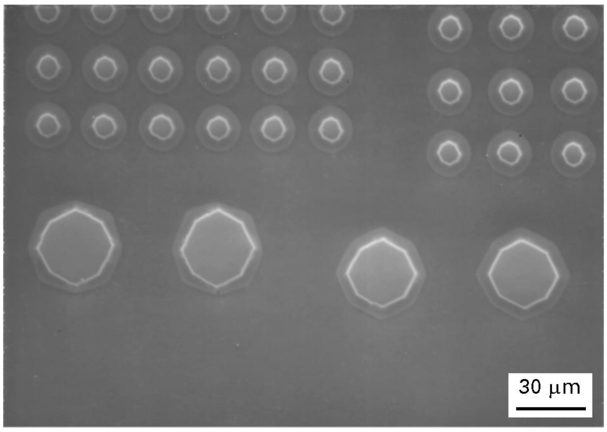


Figure 3 Various SiO_2 mask patterns showing undercutting to {331} planes. The bright [310] octagonal outline of the intercept between undercut silicon and the oxide is clearly seen. The paler outline is the original oxide mask.

orientated to the [110] directions preferentially undercut to the {221} planes and masks orientated to the [100] directions preferentially undercut to the {331} planes. Furthermore, it is proposed that in actual fact, the corner undercutting which occurs in the case of anisotropic etching with KOH follows a progression of selective etching of various crystal planes. In the case of [100] orientated masks, this progression does not stop with either the {221} or {331} crystal planes (Fig. 4), but in fact continues on to the {311} planes also along ⟨310⟩ directions but at the much higher angle of 72.45° to the (100) surface (Fig. 5).

An example of this can be seen in Figs 6–9. In this case, the corners have initially undercut to {331} planes, which have then broken down and given way to the much steeper {311} planes. The structure is finally reduced to a micro-tip with a very high aspect

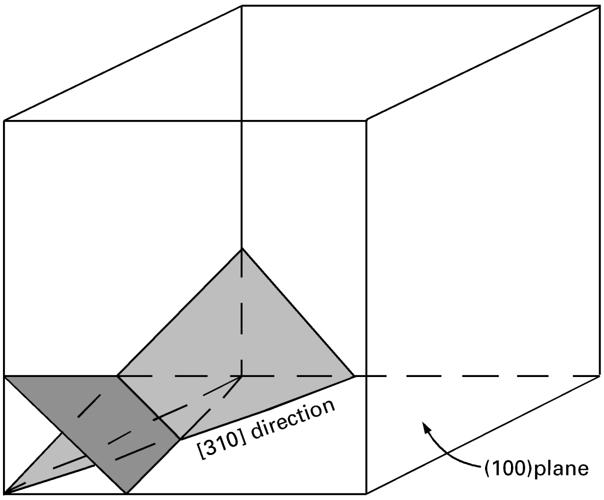


Figure 4 Two of the set of {331} planes.

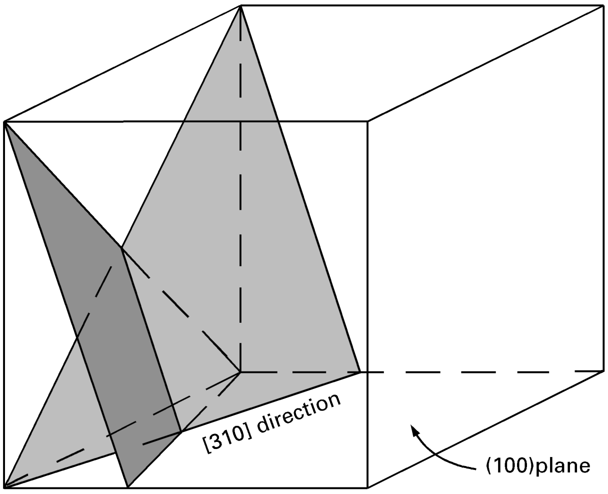


Figure 5 Two of the set of {311} planes.

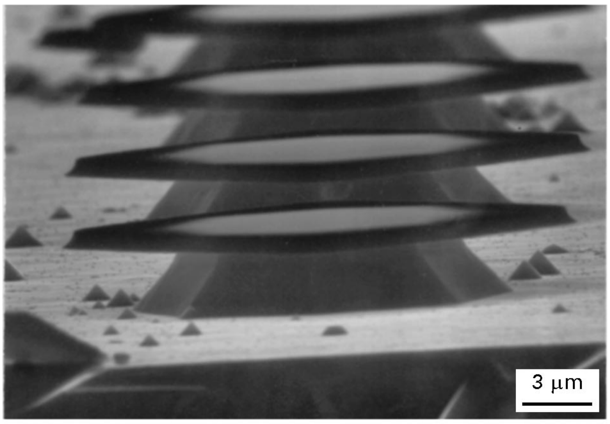


Figure 6 SEM Photo showing initial corner undercutting to the {331} planes (KOH, 2 min).

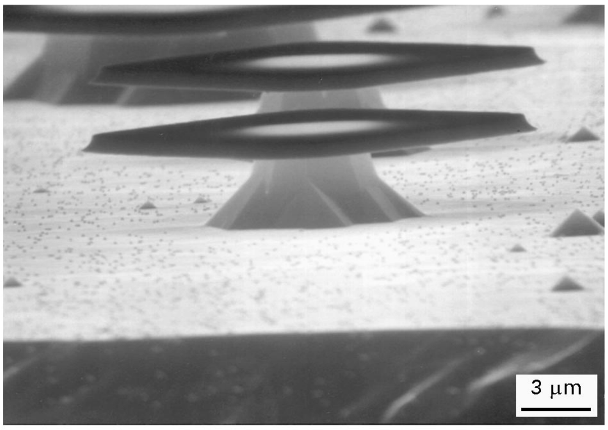


Figure 7 SEM Photo showing breakdown of the {331} planes and the formation of {311} planes (KOH, 2.5 min)

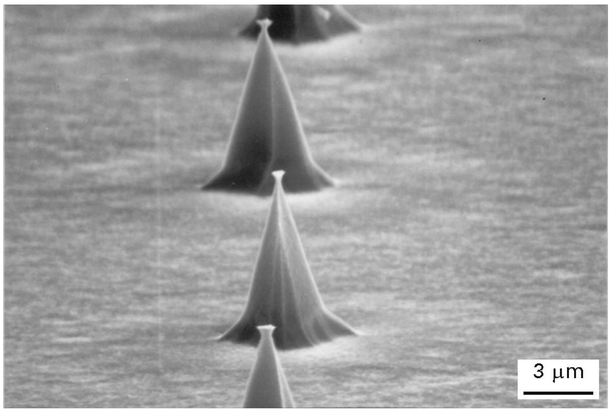


Figure 8 SEM Photo showing termination of etching at {311} planes (KOH, 4.5 min)

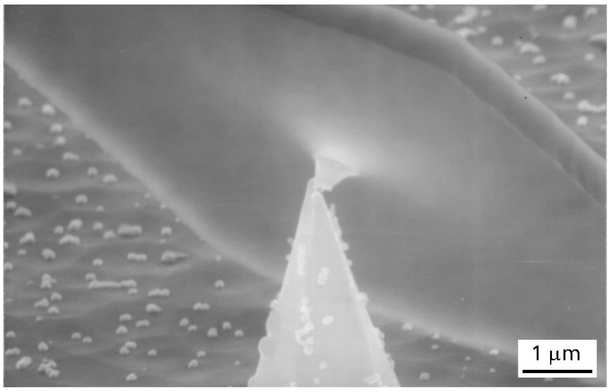


Figure 9 SEM Photo showing close-up of high aspect ratio micro-tip formed from {311} planes.

TABLE I Summary of etch results from SEM observations

Etchant type	Time (min)	Height (μm)	Vertical etch rate (μm per min)	Aspect ratio	Horizontal etch rate (μm per min)
KOH	2.0	2.1	1.1	–	1.8
KOH	2.5	2.4	1.0	–	2.0
KOH	3.0	2.8	0.9	–	1.8
KOH	3.5	3.6	1.0	0.84	1.9
KOH	4.5	4.7	1.0	1.38	–
EPW	4.5	4.2	0.9	0.53	1.1
NWH	1.25	4.5	3.6	–	4.9

ratio. Note the anomalous silicon remnants in the form of a small inverted tip near the silicon/SiO_2 interface (Figs 8 and 9). It is proposed that this is formed due to the reduction in etch rate through the reduced supply of etchant into the narrow "crevice" formed between the silicon and silicon-dioxide. Furthermore, this may be the triggering factor into the formation of the higher aspect $\{311\}$ planes. However, the point at which the $\{331\}$ planes begin to give way to the $\{311\}$ planes appears to be not easily predicted, and experimentation has shown that the $\{331\}$ planes may not always be fully removed.

Fig. 9 shows an emitter tip removed from the etch solution just prior to full removal of the SiO_2 mask cap, which has fallen off post processing. Once removal of this cap occurs, the emitter tip continues to etch rapidly, lowering the aspect ratio of the tip. Allowing the solution to etch past the point of SiO_2 cap removal can cause non-uniformity in the sharpness of the tips as the caps are removed, therefore best results are achieved by etching to a point just prior to cap removal, then using a tip sharpening method of repeated oxidation and oxide etching [13].

Table I shows a summary of etching results. It can be seen that the horizontal etch rate (through $\{221\}$, $\{331\}$, and other planes) is almost twice that for the vertical direction (i.e., the (100) plane). In contrast to the reduced etch rate of $\{111\}$ planes causing structure formation in concave structures, this increased etch rate is understood to be the cause of structure formation in the convex case. Similar comparisons of etch rate have been previously recorded by Bean and Lawson [14] and Bean [11]. Furthermore, the initiating factor in the formation of the $\{311\}$ planes is believed to be due to the reduction of this etch rate – not because of the crystal structure or bond strength – but primarily from the reduced supply of etchant to the surface of the planes near the Si/SiO_2 interface.

3.2. Etching with EPW

In stark contrast, results obtained using EPW do not show the tendency to etch to either the $\{331\}$ nor the $\{311\}$ planes. In fact, EPW consistently etched back to the $\{221\}$ planes and no further – irrespective of whether the mask was oriented to the [100] or [110] direction. Once corner undercutting occurred back to the $\{221\}$ planes, the octagonal-pyramid shape formed was maintained up to and after removal of the oxide cap. This is highlighted in the above SEM photograph (Fig. 10). It is possible that EPW does not suffer the effects of reduced etchant supply in the same manner as KOH.

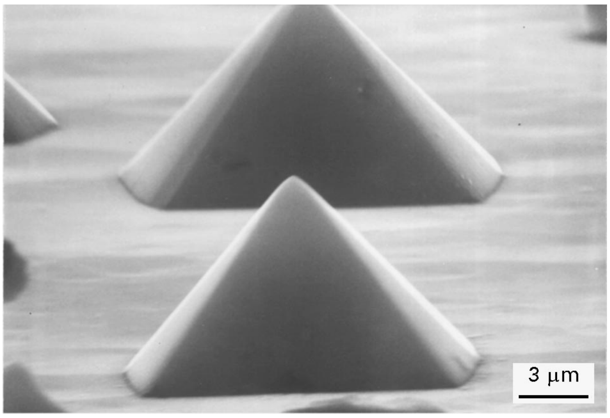


Figure 10 SEM Photo of EPW etched structure after removal of oxide cap (4.5 min).

3.3. Two step etching with KOH and NWH

Fig. 11 represents the result of the two step etched micro-tips etched for 2.5 min in 40 % KOH and followed by etching in NWH for 30 s. We define the aspect ratio as the ratio of the tip height to the width of the tip base, and compare this result with isotropically etched micro-tips. The isotropic only etched micro-tip has a 5 μm height and the aspect ratio of the micro-tip is about 0.5, as compared to the two-step etched micro-tip which is 4.7 μm in height and has an 0.8 aspect ratio. In the latter instance, the width of the tip base is strongly dependant on the anisotropic etching time. With increasing etching time in KOH, the width of the tip base decreased but the height of the micro-tip remains nearly constant. The function of the KOH is to form the basic high aspect ratio pyramid shape which is then sharpened and formed into the familiar concave micro-tip by the NWH isotropic etchant.

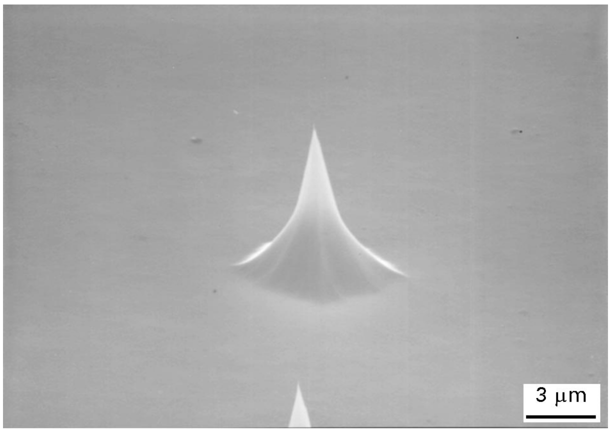


Figure 11 Two-step etched micro-tip, using 40% KOH for 2.5 min then NWH for 30 s.

In addition to the production of a high aspect ratio device, the anisotropic etching process has the added advantage of reducing the radius of the apex of the micro-tip. This reduction has been observed to be as much as 60%, giving an effective reduction from approximately 50 nm for an isotropically etched structure to approximately 20 nm for an anisotropically (KOH) etched structure, measured via observation with a scanning electron microscope.

4. Conclusion

Corner undercutting of convex masks in anisotropic etchants has been found to be dependant on both mask orientation and etchant. Using KOH, the resultant octagonal pyramid structure is formed from fast etching $\{221\}$ or $\{331\}$ planes, angled at 48° and 46°, respectively, to a (100) surface and with a similar appearance. Selection of the $\{221\}$ or $\{331\}$ bounded structure can be achieved by orientation of the mask to the [110] or [100] directions, respectively. Furthermore, continued etching results in the appearance of high aspect ratio $\{311\}$ planes at 72° to the (100) surface. It is speculated that the formation of these $\{311\}$ planes is triggered by the reduced etch rate beginning near the Si/SiO_2 interface due to the reduced supply of etchant in this area. The same patterns etched with EPW are found only to etch to $\{221\}$ planes and is independent of mask orientation. This would indicate that the EPW solution has ample supply of reactive component such that reduced flow into the crevices does not appear to reduce the etch rate.

The high aspect ratio structures formed by continued etching in KOH have significant application to the production of silicon micro-tips for use in vacuum microelectronics and field emission devices. The shape of these structures can be further enhanced by using a two-step etching process. KOH can be first used to form the basic pyramidal shape of the micro-tip, which is then sharpened further by isotropic etching in NWH. Using such a process, very sharp, high aspect ratio devices can be produced, giving improved performance for field emission devices.

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