

The Etching of Silicon Nitride in Phosphoric Acid with Silicon Dioxide as a Mask

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This article, on Phosphoric Acid etching of Nitride layers, is presented to our AccuBath customers in the hope that they will find the information it contains of practical use in optimizing their semiconductor processing.*

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ABSTRACT

The water content of phosphoric acid in etching silicon nitride and silicon dioxide plays an important role. An increase in water content increases the etch rate of silicon nitride and decreases the etch rate of silicon dioxide. The highest possible temperature for a fixed water content at atmospheric pressure in the system $H_2O-P_2O_5$ is realized by boiling the liquid and refluxing the vapor phase. Refluxed boiling phosphoric acid at $180^\circ C$ was found to be a useful etchant for silicon nitride films. The etch rate is $100 \text{ \AA}/\text{min}$. Under the same conditions deposited silicon dioxide had an etch rate of $0-25 \text{ \AA}/\text{min}$ depending on the method of preparation, and elemental silicon $3 \text{ \AA}/\text{min}$. Etch rates of silicon nitride, silicon dioxide and silicon in refluxed boiling phosphoric acid were measured as a function of temperature (and concentration) in the range of $140^\circ-200^\circ C$. All etch rates increased with temperature. The "apparent" activation energies are 12.7, 27.6, and 26.4 kcal/mole, respectively. The etch rate of silicon nitride in phosphoric acid of constant concentration (94.5% H_3PO_4) was measured as a function of temperature only. In this case, the "real" activation energy was 22.8 kcal/mole. The difference in etch rate between silicon nitride, deposited silicon dioxide, and silicon offers a technique for etching contact holes in silicon nitride using deposited silicon dioxide as a mask. Such a technique was used successfully in making transistors with silicon nitride over SiO_2 as a junction seal.

A good deal of attention has recently been focused on silicon nitride (Si_3N_4) as a semiconductor junction seal, partly or fully replacing silicon dioxide. The reason for this is that Si_3N_4 is a better mask than SiO_2 against diffusants of all kinds, including water, oxygen and sodium. The better masking properties of Si_3N_4 go hand-in-hand with lower etch rates in HF or buffered HF. Silicon nitride films prepared by various deposition processes ($SiCl_4 + NH_3$, $SiH_4 + NH_3$ and d-c plasma) were reported to exhibit "very slight" diffusion of sodium (1). These films all had low etch rates in buffered HF¹ ($\sim 10 \text{ \AA}/\text{min}$). This meant that new ways of etching contact holes had to be developed because photoresist material, now used for etching SiO_2 , does not mask sufficiently against buffered HF at the excessively long etching times necessary (2 hours for a film 1200 \AA thick). Silicon nitride films have a reasonably fast etch rate ($200-300 \text{ \AA}/\text{min}$) in concentrated HF (48%), but it was found that the ordinary photoresist materials, as used for SiO_2 , do not mask sufficiently against the concentrated HF. Even if a good etching mask for concentrated HF were available, the etching of a contact hole in Si_3N_4 which is deposited on an SiO_2 film will present the problem of undercutting because the underlying SiO_2 is etched much faster than Si_3N_4 in concentrated HF.

¹ Composition: 40g NH_4F + 80 ml H_2O + 15 ml 48% HF

This paper reports etching experiments with Si_3N_4 , SiO_2 , and Si in phosphoric acid. It was found that Si_3N_4 has a high etch rate in refluxed boiling phosphoric acid, compared to SiO_2 and elemental Si. Accordingly, phosphoric acid can be applied as an etchant for Si_3N_4 using deposited SiO_2 as a mask.

Etching Conditions

The silicon nitride films for the etching experiments with phosphoric acid were deposited by use of a pyrolytic process with SiH_4 and NH_3 at 880°C . [Silicon nitrides prepared by a d-c plasma process (2) and by a process using $\text{SiCl}_4 + \text{NH}_3$ at 1000°C had approximately the same etch rate in phosphoric acid as the silicon nitride prepared from $\text{SiH}_4 + \text{NH}_3$.]

SiO_2 films were deposited in three different ways as follows:

1. $\text{SiCl}_4 + \text{H}_2 + \text{O}_2$ at 880°C
2. $\text{SiH}_4 + \text{N}_2 + \text{O}_2$ at 350°C
3. Same as No. 2 but densified for 20 minutes in O_2 at 800°C

Film thickness was measured interferometrically with a Perkin-Elmer 202 spectrophotometer in the ultraviolet and visible wavelength range. A detailed description of the technique is given by Reizman and van Gelder (3). Reference (3) also gives the refractive index of the Si_3N_4 films as a function of wavelength. At $\lambda = 5460\text{\AA}$, the refractive index was 1.97.

A few tests were made to determine the etch rate of silicon in phosphoric acid. Silicon slices for this purpose were 58 ohm-cm p-type and were mechanically polished on both sides. The etch rate was determined by weighing on a microbalance before and after etching. In one case (at 180°C) a silicon slice half covered with SiO_2 was etched for 2 hours. The SiO_2 was then removed, aluminum was evaporated, and the step height in the silicon was measured with a multiple beam interferometer. The two methods agreed to within $\pm 10\%$.

At first the phosphoric acid was kept in an open beaker at 200°C . The acid was initially 85% H_3P_4 by weight and was slowly heated from room temperature to 200°C . The etching process was started after the acid had reached a constant temperature of 200°C for one hour.

At that point, most of the water in the acid had evaporated (partly by boiling), but the acid was not necessarily in equilibrium with atmospheric moisture. It was, in fact, observed that the Si_3N_4 etch rate was slowly decreasing with time, which was explained by assuming that the acid was still losing water. According to Brown and Whitt (4) the vapor phase in equilibrium with phosphoric acid up to 250°C is virtually pure water (0.03% P_2O_5 at 250°C). Figure 1 gives the vapor pressure of phosphoric acid solutions versus temperature for various concentrations. This figure shows, for instance, that phosphoric acid containing 75.3% P_2O_5 has a vapor pressure of 37 mm Hg at 200°C . This means that even a highly concentrated phosphoric acid of 75.3% P_2O_5 will still lose water when kept in an open beaker at 200°C because the water vapor partial pressure in a normal atmospheric ambient of 25°C and 50% relative humidity is 12mm Hg.

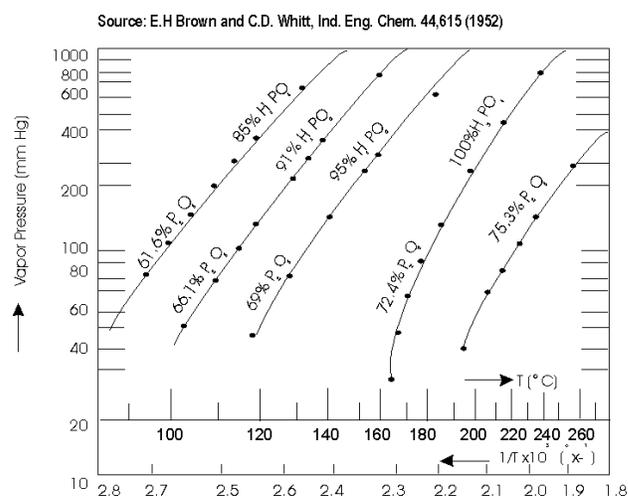


Figure 1. Vapor pressure of phosphoric acid vs. temperature for various concentrations

To overcome the problem of keeping the acid concentration at a constant and known value, later etching experiments were done with boiling phosphoric acid at atmospheric pressure and at constant temperatures ranging from 140° to 200°C with emerging water vapor constantly being condensed and returned to the boiling acid. Under these refluxing conditions, the acid remains at a constant temperature and concentration. The slices were held in a quartz basket. The "boiler" was a quartz 1-liter round-bottom flask provided with a thermometer well, a reflux

water-cooled condenser, and a wide, ground-glass tapered connector to admit the basket with slices.

Figure 1 is basically a part of the pressure-temperature diagram of the two component system $\text{H}_2\text{O}-\text{P}_2\text{O}_5$. The concentration of phosphoric acid can best be expressed in terms of weight per cent P_2O_5 . However, for commercially available phosphoric acid, the concentration is given as weight per cent H_3PO_4 . The concentrations in Figure 1 are therefore expressed both in per cent P_2O_5 and in per cent H_3PO_4 . Applying Gibbs's phase rule to the system $\text{H}_2\text{O}-\text{P}_2\text{O}_5$ for the two phases liquid and gas in equilibrium, we find that there are two degrees of freedom. This means that, of the three variables - pressure (p), temperature (T), and concentration (x) - we can only choose two while the third variable is fixed when the choice is made. For instance, the highest concentration of commercially available phosphoric acid is 85% H_2PO_4 . This liquid boils at 154°C (see Figure 2) or, in other words, at 154°C , its vapor pressure is 760 mm Hg (see Figure 1).

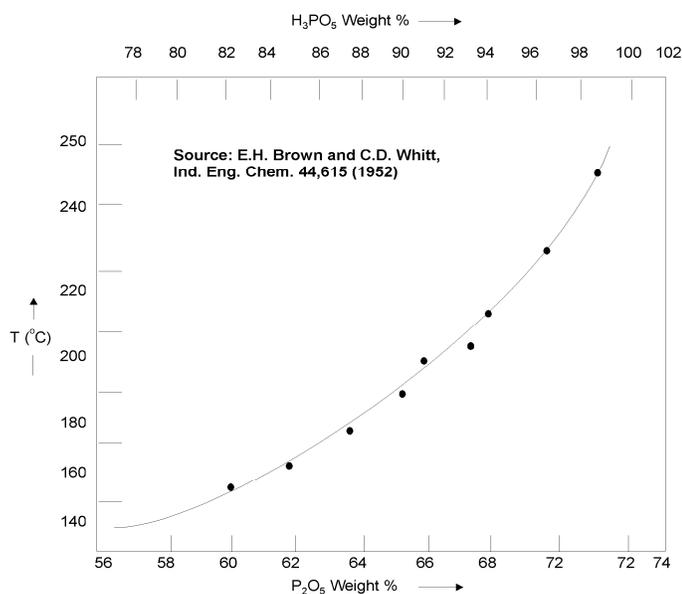


Figure 2. Boiling point of phosphoric acid at 760 mm Hg vs concentration

If the boiling liquid is totally refluxed, we have chosen the vapor pressure to be constant at 760 mm Hg (or whatever the local barometric pressure is) and the concentration at 85% H_3PO_4 . Consequently, the temperature as the third variable, is fixed at 154°C and cannot

change unless p or x is changed. The higher boiling phosphoric acids in this work were obtained by letting some water vapor escape and the lower boiling acids were obtained by adding water.

In addition to measuring the etch rates as a function of the boiling temperature (and therefore necessarily also as a function of the concentration) the etch rate of silicon nitride was measured as a function of temperature only, at a constant concentration of 94.5% H_3PO_4 . Refluxed boiling phosphoric acid at 200°C has a concentration of 94.5% H_3PO_4 . This acid was cooled down and held at 158°C and 140°C to measure the etch rate. Care was taken to let no water vapor escape. It should be noted that, in the case of refluxed boiling acid, the temperature is controlled by the amount of water in the system and not by the amount of heat put into the system.

Results

Table 1 on the next page shows results of etching experiments with Si_3N_4 and SiO_2 , comparing "open beaker" phosphoric acid at 200°C with refluxed, boiling phosphoric acid at 200° and 180°C . It is shown that the etch rate of Si_3N_4 was increased by a factor of 6 in going from open beaker acid to refluxed acid at 200°C . A factor of 2.2 was observed in the opposite direction for SiO_2 (deposited from SiCl_4 , O_2 and H_2 at 880°C). In other words, at a constant temperature of 200°C , an increase in water content caused an increase in the etch rate of silicon nitride and a decrease in the etch rate of silicon dioxide.

The etch rates of Si_3N_4 , SiO_2 and Si in refluxed boiling phosphoric acid were measured as a function of boiling temperature and are represented in Figure 3 by the solid lines. Note that the acid concentration necessarily varies with the boiling temperature. An increase in boiling temperature goes together with an increase in acid concentration and vice-versa as indicated by the abscissas of Figure 3. The slope of the Si_3N_4 line in Figure 3 is smaller than the slope of the SiO_2 line because the water content affects the etch rate of Si_3N_4 and SiO_2

Table 1. Etch rates of Si₃N₄ and SiO₂ in H₃PO₄ (Å/min)

Type of Film	Si ₃ N ₄	SiO ₂	SiO ₂	SiO ₂	Acid concentration at P ₂ O ₃
Method of film preparation	SiH ₄ - NH ₃ (880°C)	SiCl ₄ + O ₂ + H ₂ (880°C)	SiH ₄ + O ₂ 350°C Not densified	SiH ₄ - O ₂ 350°C Densified at 800°C	
Open beaker H ₃ PO ₄ @200°C	30	70	250	Not measured	>75.3% (>100% H ₃ PO ₄)
Refluxed boiling H ₃ PO ₄ 200°C	178	32	Not measured	Not measured	68.5% (94.5% H ₃ PO ₄)
Refluxed boiling H ₃ PO ₄ 180°C	105	10	25	0	66.4% (91.5% H ₃ PO ₄)

in an opposite direction. The “apparent” activation energies derived from the straight solid lines in Figure 3 are 12.7, 27.6 and 26.4 kcal/mole for Si₃N₄, SiO₂, and Si, respectively.

Figure 3 also shows a dashed line drawn through three points. This represents the etch rate of silicon nitride as a function of temperature only, at a constant concentration of 94.5% H₃PO₄. The “real” activation energy is 22.8 kcal/mole. The much steeper slope of the dashed line confirms that, at one particular temperature, a higher water content causes a higher etch rate for silicon nitride. It is apparent that SiO₂ is quite suitable as a masking layer for Si₃N₄ films against attack by the boiling phosphoric acid.

Since standard photoresist masking techniques can be used to open windows in an oxide film that has been deposited on top of a Si₃N₄ film, it is possible therefore, in turn, to dissolve out Si₃N₄, which lies exposed in the opened window areas by use of refluxed boiling phosphoric acid. If the Si₃N₄ is deposited on SiO₂, the SiO₂ can in turn be dissolved with buffered HF using the Si₃N₄ as a mask. It appeared that steam-grown SiO₂ has about the same low etch rate as Si in refluxed boiling phosphoric acid. Undercutting of SiO₂ below the Si₃N₄ did occur to a certain extent, but it did not present a problem in making contacts to transistors if the SiO₂ layer is not too thick (<6000Å). As can be seen from Figure 3, a temperature of 180°C appears to be a good choice, since it combines reasonably fast dissolution of Si₃N₄ with very little attack on the masking SiO₂ layer.

Mechanism

Water has been found to play a vital role in various etching processes. For instance, Finne and Klein (5) found that water is an active component in their amine-catechol etchant for silicon, generating hydroxyl ions in the amine solvent system. The hydroxyl ions supposedly “...oxidize the silicon to a hydrated silica [which] ...is then brought into solution by coordination with pyrocatechol which serves as a chelating agent for the silica in the presence of the amine solvent.” Hu and Kerr (7), as another example,

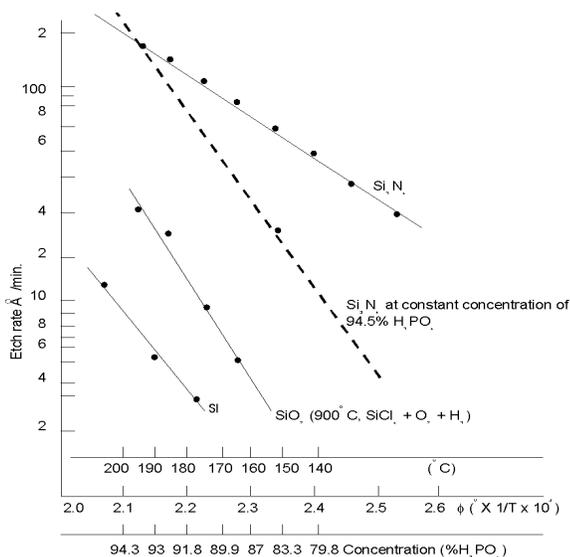


Figure 3. Solid lines: etch rate of Si₃N₄, SiO₂, and Si in refluxed boiling phosphoric acid at atmospheric pressure as a function of boiling temperature and acid concentration. Dashed line: etch rate of Si₃N₄ at a constant concentration of 94.5% H₃PO₄ as a function of temperature only.

found that dilute HF etches silicon faster than concentration (48%) HF.

An exact mechanism for the etching process of Si_3N_4 in phosphoric acid and for the role of water is not given here. It is suggested, however, that the water is essential in hydrolyzing the Si_3N_4 to some form of hydrous silica and ammonia, the ammonia remaining in solution as ammonium phosphate. The low etch rate of SiO_2 in boiling H_3PO_4 at 180°C could be explained by the fact that the Si-O-Si bond is stronger than, and not as easily hydrolyzed as, the Si-N bond. With regard to the "open beaker" method, it should be noted that concentrated phosphoric acids obtained by boiling off water from orthophosphoric acid (or by adding P_2O_5 to it) are members of a continuous series of amorphous condensed phosphoric acid mixtures, extending from orthophosphoric acid (H_3PO_4) via pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) and metaphosphoric acid (HPO_3 to pure P_2O_5) (6). Accordingly, it is suggested that the high temperature, low water content acid attacked SiO_2 faster than Si_3N_4 because a soluble phosphorus-silica complex was formed between the "poly" phosphoric acid and the SiO_2 in which the Si-O bonds are largely preserved.

Remarks, Conclusions and Recommendations

Refluxed boiling phosphoric acid at 180°C was found to be a convenient etchant for Si_3N_4 films. The etch rate is of the order of $100\text{\AA}/\text{min}$. Deposited SiO_2 can be used as a mask. Its etch rate under the same conditions is approximately $10\text{\AA}/\text{min}$, depending on the deposition temperature. Many silicon planar transistors were made using this technique to etch contact holes in Si_3N_4 films. Delineation of contact holes is good. Holes with a width of 5μ are easily produced.

For Si_3N_4 and SiO_2 , it was found that the water content of the phosphoric acid plays an important role. At constant temperature addition of water increased the etch rate of Si_3N_4 and decreased the etch rate of SiO_2 . The maximum possible temperature at atmospheric pressure for a fixed water content was realized by boiling the acid and "refluxing" the vapor phase.

For safe operation of the etching bath, boiling aids such as Teflon-coated stirring bars should always be used.

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