# VLSI Fabrication Principles

## Silicon and Gallium Arsenide

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### 9.1.6.3 Mixed Oxides

These include* borosilicate glass (BSG) as well as $ZnO \cdot SiO_2$ and $SnO_2 \cdot SiO_2$. All are useful as dopant sources. The BSG is used as a *p*-type doped oxide source for silicon, whereas $ZnO \cdot SiO_2$ and $SnO_2 \cdot SiO_2$ are used as *p*- and *n*-type dopant sources for gallium arsenide, respectively. They are grown at 350–450°C, by the simultaneous oxidation of silane and the appropriate dopant hydride or alkyl (diborane, diethylzinc, and tetramethyltin, respectively). They can be readily etched in HF, or in BHF since $SiO_2$ is their primary constitutent. Again, etching proceeds by the dissolution of the $SiO_2$ in the HF, rendering the structure porous and thus more susceptible to dissolution.

Dilute BHF is commonly used with these doped oxides. Its dissolution of BSG has been investigated in some depth [42]. Typically, the etch rate is seen to increase monotonically with the $B_2O_3$ content. In some instances, however, anomalous characteristics have been observed during the etching of BSG films.

A thin layer of BSG is also formed during the boron doping of masked silicon wafers. Selective etches, known as R-etch and S-etch, can be used [44] to remove this film while leaving the underlying $SiO_2$ unetched. Both etches are modifications of the P-etch formulation; typically they are about five to six times more rapid in their ability to remove the BSG layer.

The etch characteristics of both $ZnO \cdot SiO_2$ and $SnO_2 \cdot SiO_2$ have not been studied. However, they are comparable to undoped $SiO_2$ grown by the silane process. Dilute BHF has been found useful for this purpose.

### 9.1.6.4 Silicon Nitride

Silicon nitride (commonly written as SiN) is an inert dense material which is an excellent diffusion barrier to both sodium and gallium. For this reason, it is widely used as a protective coating for silicon microcircuits, and also as a cap during the annealing of ion-implanted gallium arsenide. Its protective characteristics are generally superior to those of $SiO_2$ and PSG. However, its patterned removal is more difficult and is highly dependent on the growth technique.

Both HF and BHF can be used to etch these films [45]. However, even at elevated temperatures, the etch rates are extremely slow, so that photoresist films are ruined during this process. Typically, the etch rate of CVD films ($SiH_4/NH_3$ process) is a function of the growth temperature [46]. The etch rate is concentrated HF is about 1000 Å/min for films grown at 800°C, falling to as low as 140 Å/min for films grown at 1100°C. The etch rate in BHF is considerably lower, about 5–15 Å/min for films grown at 1100°C.

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* PSG belongs in this category as well. However, it has been treated separately because of its importance in microcircuit fabrication technology.

The problem of photoresist destruction can be avoided by depositing a molybdenum film between the nitride and the photoresist. This film can be readily etched with excellent edge definition by standard photolithographic techniques. Once patterned, it can be used as a mask for etching the underlying SiN film, after the resist has been stripped.

Silicon nitride is often used as a cover layer over a film of silica. In these situations, neither HF nor BHF can be used, since this would result in deep undercutting of the $SiO_2$ layer, which is etched rapidly by these solutions. Instead, etching is carried out in boiling* $H_3PO_4$, and a reflux boiler apparatus is used to avoid changes in the etchant composition during this process. Typically [47], the etch rate for CVD grown SiN films is about 100 Å/min, while the etch rate for thermally grown $SiO_2$ layers is about 10–20 Å/min. For these same conditions, the etch rate of silicon is under 3 Å/min, so that this technique can be used in the presence of exposed silicon surfaces. A curve of comparative etch rates of these films is shown in Fig. 9.8.

There are many situations in which consecutive layers of SiN and $SiO_2$ must be etched at the same rate (the gate oxide of a metal–nitride–oxide semiconductor (MNOS) field effect transistor, for example). Here mixtures of HF and glycerol are used at 80–90°C, and experimentally adjusted to provide equal etch rates. Typically, a 1–3 mole/liter concentration of HF etches $SiO_2$ and CVD SiN films at equal rates of about 100 Å/min at 80°C [48].

The etch rate of SiN films is extremely sensitive to the incorporation of even trace amounts of oxygen in them. In general, the etch rate in HF and BHF increases with oxygen incorporation, whereas the etch rate in $H_3PO_4$ decreases. Typically, the etch rate in concentrated HF varies [46] from 350 Å/min for $Si_xO_yN_z$ films grown at 1000°C with 7% $SiO_2$ incorporated in them, to as high as 5000 Å/min for films with 50% $SiO_2$ incorporation. Also, it should be noted that SiN films, grown at low temperatures by plasma-enhanced CVD (see Chapter 8), contain a large amount of incorporated hydrogen and have considerably faster etch rates than those grown by conventional techniques.

### 9.1.6.5 Polysilicon and Semi-Insulating Polysilicon

The same chemical systems used for etching silicon can be used for both undoped and doped polysilicon. In general, their etch rate is considerably faster, so that their use results in films with poor edge definition. However, these etches can be modified to be suitable for polysilicon. This usually consists of greatly reducing the amount of HF, using large ratios of $HNO_3$ to HF, and large amounts of diluent. Typical etch rates for these formulations are about 1500–7500 Å/min for undoped films. Etch rates for doped films are strongly dependent on the crystallite size and the doping concentration.

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* The etching temperature is thus related to the concentration of the $H_3PO_4$.

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