Chapter 5
Wet Etching

5.1 INTRODUCTION

Wet etching is the use of liquid etchants to remove material. Such etching procedures are important parts of various processing steps. Gallium arsenide is etched to remove damaged material, to form mesa structures for device isolation (Chapter 10), to recess gates in FETs (Chapter 12), to aid in polishing, as part of cleaning procedures, or as an integral part of diagnostic techniques. Other materials, such as metals and dielectrics, may be etched as part of device fabrication procedures. There are other important etching techniques in addition to wet etching. These are described in Chapter 9 (dry etching). Etching of GaAs is the main topic of this chapter, and will be considered in detail in Sections 5.2 and 5.3. Discussion of electrically aided wet etching (anodic or cathodic etching) is included. Section 5.4 discusses wet etching of other materials likely to be used in GaAs processing.

Wet etching proceeds through chemical reactions that occur at the surface of the material. In order for these to take place, the etchant species must reach the surface, the appropriate reactions must occur, and the resulting products must be removed from the surface. One of two basic mechanisms limits the dissolution rate. First, the etch rate may be controlled by the rate at which reactant species can reach the surface (or the rate at which reactant products can be removed). This situation is referred to as *diffusion-limited* or *mass-transport-limited* etching. This is a common occurrence because the diffusion coefficient of species in liquids is very small, on the order of 10^{-9} m^2/s [1]. Second, the etch rate may be limited by the rate of chemical reactions occurring on the surface. This situation is referred to as *reaction-rate-limited, surface limited,* or *kinetically limited* etching. The limiting regime is a function of etch composition and temperature.

Diffusion- or mass-transport-limited etchants tend to be more isotropic with respect to crystal orientation, so they tend to give a more polishing effect. This occurs because surface protrusions are more available to incoming species, and tend to be etched more rapidly than a smoother surface. Because agitation can greatly

affect mass transport, etch rates may be highly sensitive to the form and degree of agitation.

Reaction-rate-limited etches tend to preserve surface morphology, although this tendency can be completely dominated by a second tendency: to be highly anisotropic in selectively etching crystalline structures through masking patterns. These etchants are much less sensitive to agitation.

As with all chemical reactions, etching is sensitive to temperature. A 10° C increase in temperature can increase etch rate by a factor of two. Freshly mixed etchants may be hot. Etching that occurs in a small volume of solution can cause its temperature to increase during the etching process. Compound etchants may change composition over time, depending on temperature and storage technique. All these effects must be considered in establishing reproducible and controllable etching processes.

Some etching conditions may produce bubbles, usually hydrogen, which can adhere to the surface being etched and cause nonuniform etching. This can be alleviated by agitation or use of surface-active (wetting) agents.

5.2 BASIC CONSIDERATIONS IN GaAs ETCHING

Section 5.1 described several fundamental considerations that apply to wet etching in general. Further generalizations can be made about wet etching GaAs. The zincblende crystal structure of GaAs (Chapter 2) leads to etching characteristics that are very different from those of silicon. General reviews of GaAs etching may be found in [2–6]. Papers treating wet etching of GaAs and other semiconductors may be found in the *Journal of the Electrochemical Society*.

Almost all GaAs etchants operate by first oxidizing the surface and then dissolving the oxide, thereby removing some of the gallium and arsenic atoms. Generally, the etchant will contain one component that acts as the oxidizer and another that is the dissolving agent. The popular etchant H_2SO_4-H_2O_2-H_2O is an excellent example. The hydrogen peroxide is the oxidizing agent; sulfuric acid dissolves the resulting oxide. In appropriate proportions, this etchant rapidly dissolves GaAs. Although it etches GaAs to some degree in almost all proportions, GaAs will not etch in either H_2O_2 or H_2SO_4 alone.

The oxidation is essentially an electrochemical process in which localized anodic and cathodic sites are believed to exist at the semiconductor surface. Oxidations occurs at anodic sites and the oxidant is reduced at cathodic sites [3, 4, 7]. The electrochemical nature of the process makes it sensitive to any mechanism that can supply (or restrict) electrons or holes at the surface [3, 4]. Examples of such mechanisms are illumination [8] and electrical currents [9–11]. Both anodic and cathodic etching will be considered in Section 5.3.

The crystalline nature of the GaAs lattice leads to anisotropic etching in almost all cases in which masking materials are used to pattern the wafer for etching. This

generality may be illustrated by considering a specific example based on (100) wafer orientation (see Section 2.2 for a discussion of the nomenclature used to designate crystallographic directions and planes). This is by far the most commonly used wafer orientation for device fabrication and, as explained in Chapter 2, has two natural cleavage directions perpendicular to each other. These are the {110} planes. Devices are generally oriented parallel to these planes to allow scribing or to minimize problems in sawing when the wafer is cut into separate chips. Figure 5.1 illustrates the anisotropic etching behavior generally obtained on such material. The squares in the figure represent mesas formed by etching away material outside of the square. A masking material, such as photoresist, can be used to project the mesa area from the action of the etchant. The figure indicates the general nature of edge profiles that will result from using most etchants. In Figure 5.1(a), the mesa has been oriented so that its edges are parallel to a ⟨011⟩ direction. In this case, two of the edges will yield profiles that have outward slopes; the other two edges will have inward sloping or undercut profiles. Obviously, one direction is completely inappropriate for metal crossovers. Such considerations must be anticipated in device design and fabrication (Chapter 10). In Figure 5.1(b), the mesa has been oriented so that its edges are 45° to a ⟨011⟩ direction. In this case, the resulting edge profiles will be midway between the two cases above, and will yield essentially vertical walls. However, note that, in all cases, there is considerable undercutting of the masking material. This is a major limitation in wet etching GaAs; the lateral etch rate is a significant fraction of the vertical etch rate. Achievement of low-undercut etch rates usually requires the use of dry etching procedures (Chapter 9). The profiles shown in Figure 5.1 are intended only as general representations. Specific etches (see below) will have slightly different profiles, and a few will be more isotropic.

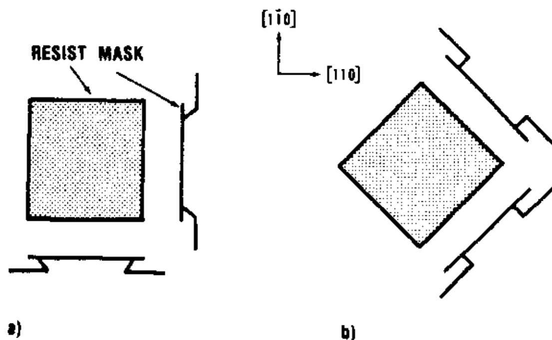


Figure 5.1 Anisotropic etching behavior typically exhibited by most wet etchants on a (100) oriented GaAs slice: (a) Mask edges are parallel to the ⟨011⟩ cleavage planes; (b) Mask edges are 45° to the cleavage planes.

The anisotropic nature of etching behavior follows from the lack of symmetry in the GaAs lattice and the dependence of etch rate on crystal orientation. The etching characteristics of GaAs tend to be dominated by the {111}*A* planes. These planes often appear in edge profiles resulting from etching through masking patterns. As discussed in Section 2.2, the {111} planes consist either of all gallium atoms or all arsenic atoms, and are referred to as {111}*A* or {111}*B* planes, respectively. The *A* and *B* planes have very different chemical properties. The differences can be understood by considering the bonding between atoms as indicated schematically in Figure 5.2. Note that the planes are bonded alternately by sets of three bonds and sets of one bond. The material will cleave between planes joined by the single bonds, rather than between the planes joined by the triple bonds. Thus, one surface will be type *A* (gallium) and the other will be type *B* (arsenic). The surface type may be identified using either x-ray or chemical means [2, 3]. The two planes joined by triple bonds may be conceived as a double sheet of atoms. A qualitative understanding of the chemical etching properties of various atomic planes may be aided by the following analysis. Assuming electrical neutrality of the surface atoms, the surface gallium atoms (plane *A*) each have three bonding electrons, and the surface arsenic atoms (plane *B*) each have five bonding electrons. Each atom is connected to the next plane by three bonds. Thus, the surface gallium atoms have no free electrons. The surface arsenic atoms have two free electrons, which are available to take part in any reaction. For rate-limited reactions, the {111}*B* surfaces are expected to etch faster than the {111}*A* surfaces. By this argument, a {100} surface, having both Ga and As atoms (with double bonds), is expected to etch at an intermediate rate. That is, the etch rate would be ordered {111}*B* > {100} > {111}*A*. This ordering has been confirmed for several materials having zinc-blende crystal structure [2], including GaAs when etched by using bromine-methanol [12].

The above description is somewhat simplistic. In practice, removal of an atom from the surface not only exposes the layer beneath, but also allows lateral attack

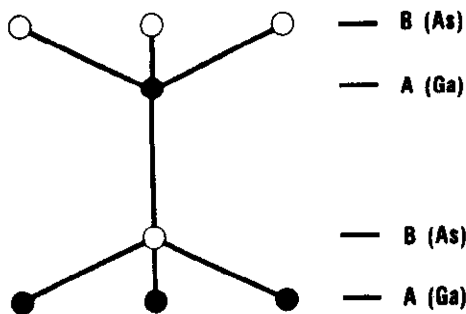


Figure 5.2 Planes of atoms alternately joined by single and triple bonds in the GaAs lattice.

of the etchant on the surface layer atoms immediately adjacent to the removed atom. This situation can lead to small-scale roughness (microfaceting) superimposed on the large-scale behavior described above [13]. Such microfaceting can make an etched surface appear cloudy to the naked eye. The smoothness of the original surface can also affect the degree of such *microfaceting,* with a rough surface generating more than a smooth surface. Diffusion-limited polishing etches are used during wafer generation and polishing to prevent this effect.

Crystal defects will also affect etch results. In fact, etching in hot KOH is a standard technique used to ascertain dislocation density. Use of nonpolishing etchants will tend to reveal defects or damage. Some of that damage may have been generated in the sawing operation when wafers were cut from the boule. Inadequate removal of damaged material or poor polishing can result in wafers that appear perfectly smooth, but reveal damage patterns when etched. Figure 5.3 shows such an example. The general relationship between etching and crystal defects is complex, and will not be pursued here. Further details may be found in Tuck [2] and Stirland and Straughan [3].

Etch profiles are also affected by factors other than those described above. There is a strong tendency for etching to result in exposure of various crystalline planes. However, this process can be affected by poor adhesion of the masking substance or diffusion effects. If the masking substance does not adhere perfectly to the water surface, the resulting profile will be affected. Unbaked photoresist is partic-

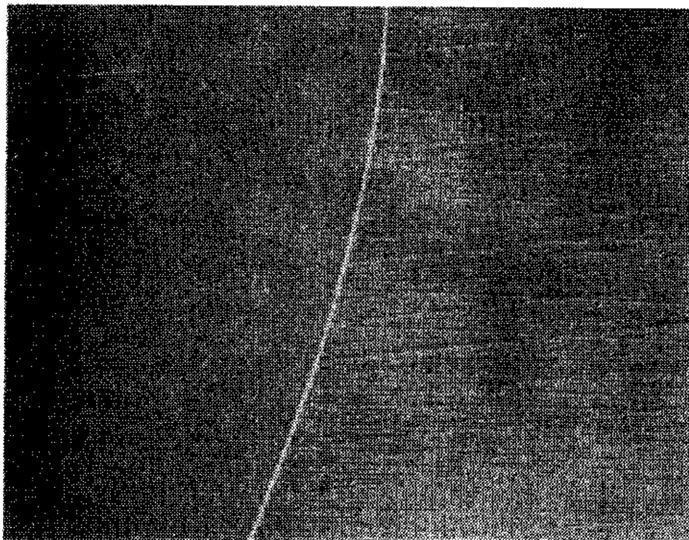


Figure 5.3 Damage revealed by etching a GaAs slice. The original surface was polished smooth, as evidenced by the adjacent area which was masked during etching.

ularly susceptible to this problem. Diffusion effects near the mask edge can also affect the exact profile obtained. This is because the most relevant criterion for faceting is not absolute etching rates of given planes, but etching rates relative to adjacent orientations [14, 15] (diffusion-limited etchants are particularly affected).

The shape of the edge profile produced by wet etching can be understood on the basis of the etch rate of specific crystalline planes. If the relative etch rate of such planes can be determined, the edge profile can be predicted. The procedure will be summarized here; a detailed description of this technique may be found in Shaw [16]. The approach is to construct normals to radius vectors, which represent the dissolution rate in a given direction. These dissolution rate vectors can be represented by a polar diagram, and the normals are then tangents to the polar figure. A facet will appear in the etch profile at any place where there is a cusp in the polar diagram. The resulting edge profile is represented by the envelope formed by the assemblage of normals. Such a construction is called a *Wulff plot*. This graphical procedure is particularly suitable for computer generated plots. The success of this approach in predicting etched edge profiles is indicated by the example shown in Figure 5.4 [16]. It shows predicted and experimental profiles obtained etching (100) GaAs in a sulfuric acid etch using patterns oriented in the two cleavage directions. We emphasize that the success of the technique depends on being able to ascertain the rate vectors which are valid for the actual process conditions. Because of effects described above, these may differ from rates obtained by using unpatterned surfaces. The usefulness of the technique is increased by the fact that sufficiently accurate polar diagrams can often be constructed on the basis of data derived from etching simple test structures [16]. Such polar diagrams can then be used to predict edge profiles when different wafer orientations or initial masking geometries are involved.

As noted above, agitation can increase etch rate, but also can hinder uniformity over a wafer unless the technique provides equivalent agitation at all points across

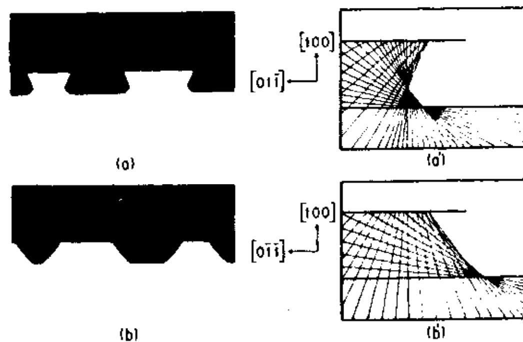


Figure 5.4 Comparison of theoretical and experimental edge profiles produced using a $H_2SO_4/H_2O_2/H_2O$ etchant (from Shaw, [16]; reproduced with permission).

the wafer surface. One technique used when high throughput is not required is to place the wafer on the bottom of a beaker of etchant that is slanted at 30° to 45° and rotated about its axis. Ultrasonic agitation is also commonly employed. A novel approach to modifying etch behavior by affecting diffusion is to etch in high acceleration fields using a centrifuge [17].

Spray etching is another method of applying etchant to the wafer that can be considered a form of agitation and has proven compatible with production environments. In this technique, the etchant solution is sprayed onto the wafer, which usually is being spun on a vacuum chuck. Deionized water is normally sprayed on immediately after the etchant to quench the etching action and rinse the wafer, after which it is spun dry (a very effective technique that prevents water "stains" on the wafer). Commercial equipment with cassette-to-cassette automatic wafer handling and microprocessor control is available for such purposes. Etch speed and uniformity are critically dependent on many parameters, including spin speed, etchant pressure and flow, and the exact characteristics of the spray nozzle. After the process is established, however, it can exhibit a high degree of reproducibility. Spray etching is becoming a common technique in production environments.

One aspect of GaAs etching will not be discussed in this book: chemical-mechanical polishing after cutting wafers from the crystal ingot. Such polishing operations are performed by using diffusion-limited polishing etchants such as bromine-methanol in combination with mechanical polishing. The reader may consult Stirland and Straughan [3] and Kern and Deckert [5] for further information on this technique.

5.3 GaAs ETCHANTS

Many etchants have been reported for etching GaAs. As indicated above, almost any combination of oxidizer and oxide-dissolver will operate as an etchant, but only a few of these systems have gained substantial popularity in GaAs device processing. We consider these major etching systems in the following subsections. A final subsection describes anodic and cathodic etching techniques.

The concentration of initial reagents used in these etching systems in shown in Table 5.1. Etchant mixtures of these reagents are indicated by the notation $n1{:}n2{:}\ \ldots$, where the numbers represent volume (not weight) ratios of the components and are ranked in the same order given in the system name. For example, in the $H_2SO_4/H_2O_2/H_2O$ system, the mixture 1:8:40 means one part sulfuric acid, eight parts hydrogen peroxide, and forty parts water (by volume).

5.3.1 The H_2SO_4-H_2O_2-H_2O System

The most popular etching system for GaAs consists of various proportions of sulfuric acid, hydrogen peroxide, and water. This etching system is often used for etch pol-

Table 5.1
Initial Concentrations of Reagents Used in Wet Etching

Reagent	*Percentage of Weight*
HCl	37
HF	49
H_2SO_4	98
H_3PO_4	85
HNO_3	70
CH_3COOH	99
H_2O_2	30
NH_4OH	29 (as NH_3)
NaOH	97

ishing substrates, mesa etching, or gate recess etching. This etchant system has been described in detail in the literature [6, 13–15].

Sulfuric acid is a rather viscous liquid. Etchants having a high proportion of sulfuric acid tend to be diffusion limited in character, and are useful for polishing. Combinations of 4:1:1 or 3:1:1 are commonly used to polish substrates and to remove surface damage. When masking patterns are present, high proportions of sulfuric acid generally result in holes having nonplanar bottoms [14, 18]. This effect is consistent with the diffusion-limited character of high-proportion sulfuric acid mixtures and the related mask edge effects noted in the previous section. Etch rate is rapid, too rapid for good control of such process steps as mesa etching or gate recess. More dilute mixtures are generally used for these purposes. Low sulfuric acid proportions produce flat-bottom holes, consistent with reaction-rate-limited behavior. The transition between "high" and "low" sulfuric acid concentrations occurs at approximately one-third sulfuric acid [14].

The relative etch rate as a function of the proportions of the components may be inferred from Figure 5.5 [14], which shows absolute etching rates obtained etching (100) material at 0° C. Note that the etch rate approaches zero as either the sulfuric acid or the hydrogen peroxide component approaches zero. In regions C and D of the diagram (high H_2O_2 and high H_2SO_4), mirror-like surfaces were obtained over a wide range of etching temperatures; cloudy surfaces resulted under some conditions in regions *A* and *B* [14]. The dependence of etch rate on temperature and agitation (using a high concentration of sulfuric acid) is indicated by the data shown in Figure 5.6 (from Iida and Ito [14]). In this case, the agitation was ultrasonic.

Various orientations of wafers have been etched using the $H_2SO_4/H_2O_2/H_2O$ system. Table 5.2 (from Iida and Ito [14]), presents these results obtained by using low-concentration sulfuric acid and indicates the profile obtained. Most processing,

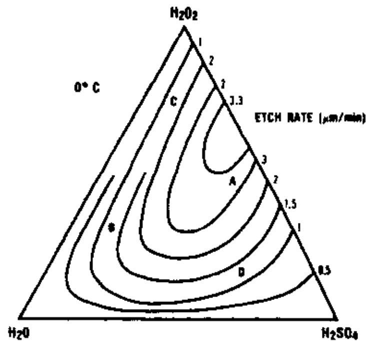


Figure 5.5 Constant etching rate contours for the $H_2SO_4/H_2O_2/H_2O$ system (after Iida and Ito, [14]).

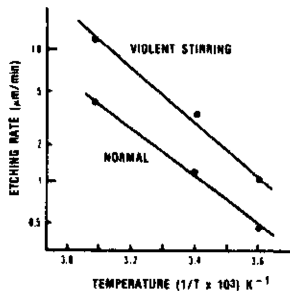


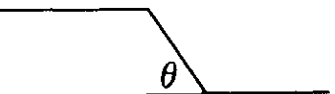
Figure 5.6 Affect of agitation on etch rate using a high sulfuric acid concentration etchant (after Iida and Ito, [14]).

however, occurs on (100) oriented wafers. Table 5.3 (from Shaw [15]) presents data for etching (100) GaAs wafers by using various proportions of the etch components. The wafers were etched at room temperature and under gentle agitation (in rotating, angled beakers). Note the flat bottoms (near the mask) formed by using low-concentration sulfuric acid mixtures.

Photoresist masks exhibit suitable adhesion for most proportions of the components, but only if the resist is baked. Personnel must also be careful about the concentration of the hydrogen peroxide. The initial reagent is usually 30% H_2O_2. However, it is often stored in bottles with a small hole in the lid to prevent dangerous pressure buildup. This situation can result in a decrease in concentration over time, especially when the bottle is nearly empty. Similarly, the prepared mixture of acid, peroxide, and water will tend to lose peroxide over time. This effect is aided by the high temperature that results during mixture of the acid with the other components.

Table 5.2
Slot Geometries Resulting from Wet Etching of GaAs
Substrates of Various Orientations (from [14])

Substrate	Window Direction	I Plane	I Angle	II Plane	II Angle
(001)	[110]	(111)	55	$(\bar{1}\bar{1}1)$	55
	[110]	$(1\bar{1}1)$	-55	$(\bar{1}11)$	-55
	[100]	(100)	90	$(\bar{1}00)$	90
	$[0\bar{1}0]$	$(0\bar{1}0)$	90	(010)	90
(111)	$[1\bar{1}0]$	$(00\bar{1})$	-55	$(\bar{1}\bar{1}1)$	-70.5
	$[11\bar{2}]$	$(\bar{3}1\bar{1})$	-58.5	$(1\bar{3}\bar{1})$	-58.5
$(\bar{1}\bar{1}\bar{1})$	$[1\bar{1}0]$	$(\bar{1}\bar{1}1)$	70.5	$(00\bar{1})$	55
	$[11\bar{2}]$	$(\bar{1}31)$	58.5	$(1\bar{3}\bar{1})$	58.5
(110)	[110]	(111)	35	$(00\bar{1})$	90
	[001]	(100)	45	(010)	45
(112)	$[1\bar{1}0]$	(111)	19.5	$(\bar{1}\bar{1}1)$	90
	$[11\bar{1}]$	$(1\bar{2}\bar{1})$	-60	$(\bar{2}1\bar{1})$	-60
$(\bar{1}\bar{1}\bar{2})$	$[1\bar{1}0]$	$(00\bar{1})$	35	$(\bar{1}\bar{1}1)$	90
	$[11\bar{1}]$	$(1\bar{2}\bar{1})$	60	$(\bar{2}1\bar{1})$	60
(113)	$[1\bar{1}0]$	(111)	29.5	$(\bar{1}\bar{1}1)$	80
	$[33\bar{2}]$	$(3\bar{5}\bar{3})$	-55	$(\bar{5}3\bar{3})$	-55
$(\bar{1}\bar{1}\bar{3})$	$[1\bar{1}0]$	$(00\bar{1})$	25	$(\bar{1}\bar{1}1)$	-80
	$[33\bar{2}]$	$(3\bar{5}\bar{3})$	55	$(\bar{5}3\bar{5})$	55



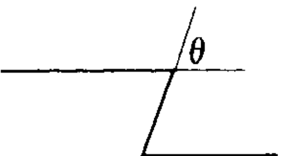


Table 5.3
Characteristics of Acidic Hydrogen Peroxide Etchants for GaAs
(from Shaw [15], reprinted by permission of the publisher, the Electrochemical Society, Inc.)

ACID	VOLUME RATIOS *	CONCENTRATION (mol/l)		RATIO OF UNDERCUT TO ETCHED DEPTH			RELATIVE ANISOTROPY	ETCH RATE (100) ($\mu m\ min^{-1}$)	CROSS-SECTIONAL PROFILES	
		ACID	H_2O_2	<01̄1̄>	<011>	<100>			(011) SECTION	(01̄1) SECTION
H_2SO_4	1:8:1	1.8	8.0	0.30	0.30	0.90	1.0	14.6		
H_2SO_4	1:8:40	0.36	1.6	0.89	0.68	1.2	0.55	1.2		
H_2SO_4	1:8:80	0.20	0.90	0.62	0.62	0.86	0.32	0.54		
H_2SO_4	1:8:160	0.10	0.47	0.71	0.71	0.93	0.27	0.26		
H_2SO_4	1:8:1000	0.018	0.079	0.82	0.76	0.95	0.22	0.038		
H_2SO_4	1:1:8	1.8	1.0	0.77	0.53	1.0	0.61	1.3		
H_2SO_4	4:1:5	7.1	1.0	0.49	0.29	0.70	0.83	5.0		
H_2SO_4	8:1:1	14.0	1.0	0.52	0.43	0.61	0.35	1.2		
H_2SO_4	3:1:1	11.0	2.0	0.44	0.44	0.53	0.19	5.9		
HCl	1:4:40	0.27	0.87	0.51	0.28	0.97	1.1	0.22		
HCl	1:1:9	1.1	0.89	0.22	0.18	0.37	0.69	0.20		
HCl	40:4:1	10.6	0.87	0.54	0.54	0.54	~0	>5.0		
HCl	80:4:1	11.2	0.46	0.7	0.7	0.7	~0	1.1		

* ACID (CONCENTRATED): H_2O_2(30%): H_2O

For this reason, a useful procedure may be initially adding the acid to the water, waiting until the mixture is cool, and then adding the hydrogen peroxide. Because of evolution of peroxide, the etchant will exhibit an exponential decrease in etch rate as a function of storage time. Most of the change occurs within 24 to 48 hours. Hence, reproducibility in etch characteristics requires that the etchant be used under restrictions. These might be using only an "aged" mixture, using a mixture within certain time spans after preparation, or storing the mixture in sealed, collapsible containers (such as are used for storing photographic developer).

Etchants that include hydrogen peroxide have a tendency to form bubbles while etching. These could cause nonuniform etching, and should be removed by agitation or prevented by use of wetting agents.

5.3.2 Bromine-methanol

The bromine-methanol (Br/CH_3OH) etchant can etch GaAs rapidly, and is useful as a polishing or smoothing etchant [3,5]. Generally, bromine-methanol is used in concentrations near 1% Br, but higher concentrations are also used, resulting in different etch characteristics. The etchant has been described throughout the literature [4, 6, 12, 19]. The system has two disadvantages. One is not a technical limitation: bromine is extremely pungent, so this etchant must be used in well-ventilated hoods. The other is more serious: bromine is highly caustic, and resist is not suitable as a masking substance. Dielectric materials must generally be used.

Bromine-methanol tends to form etched grooves that have nonflat bottoms, as shown in Figure 5.7 [6, 12]. Figures 5.8 and 5.9 illustrate the relative etch rate of various planes as a function of bromine concentration [11] (Note that the data are presented using weight percentage of bromine, in contrast to the usual practice of quoting volume percentage). The etch rate order of various planes is $\{110\} > \{111\}B > \{100\} > \{111\}A$, but (as usual) the $\{111\}A$ etch rate is significantly less than the others. The above results are for volume concentrations of Br of about 1.3% or less. At higher concentrations, different behavior is seen. Above about 5% Br, the "stop" plane (or very slow etching plane) becomes the $\{332\}$ plane instead of the $\{111\}A$ plane [19]. This affects the resulting geometries, and illustrates the complexities that can occur in wet etching. For example, consider a slot oriented in the [011] direction (the direction that yields V grooves) and slots oriented at 10° intervals from that direction. Low-concentration bromine solutions (1%) will yield the V shape only for the on-axis slot. The others will exhibit the reverse mesa shape [19], but high concentration bromine solutions (>5%) will give V-shaped slots for the on-axis and the two slots oriented away; the other slots (i.e., at 20°, 30°) will still exhibit the reverse mesa shape [19]. The center V slot will have serrulated walls. These cases are illustrated in Figure 5.10. The explanation is that the high concentration bromine etchant stops at $\{332\}$ planes and these planes form the walls of a V slot located 11.3°