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A new etchant system, $K_2Cr_2O_7$–H_2SO_4–HCl, for GaAs and InP

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A new $K_2Cr_2O_7$–H_2SO_4–HCl system has been developed that is particularly suitable for use in etching solutions of GaAs and InP. This system provides high quality etched surfaces without any undesirable roughness or etch pits. It has been found that the etching rate can be controlled by changing the etchant component proportions. This is especially the case with HCl. This leads to no change of surface quality. Vertical walls, and mesa-shaped structures have been formed on etching profiles of (001) GaAs by stripes parallel to the [110], and [$\bar{1}$10] directions, respectively. The mesa-shaped profiles have been formed for (001) InP in both the [110] and [$\bar{1}$10] directions. The solution does not erode photoresist masks and is thereby attractive for a variety of device applications.

1. Introduction

Chemical etching of semiconductors plays an essential role in electron device technology. Important factors determining the choice of an etchant are, generally, the etching rates for the materials in question, the degree of surface quality and undercutting, the solution chemical aggressiveness toward photoresist masks and the desired etching profile for the relevant purpose.

There have been many reports on the etching characteristics of GaAs [1]. The most commonly used etchants for GaAs are various compositions of Br_2–CH_3OH, H_2SO_4–H_2O_2–H_2O and $NH_4OH(NaOH)$–H_2O_2–H_2O. These solutions, however, tend to erode photoresist masks such as AZ-1350. Currently InP and related compounds such as InGaAsP are of great interest because of recent requirements of high-speed transistors, and light sources (lasers) and detectors for optical fibre communication. There have, however, been few reports on the etching characteristics for these compounds [2–5].

In this paper, a new etching solution composed of $K_2Cr_2O_7$ aqueous solution, H_2SO_4 and HCl has been developed for etching GaAs and InP. This solution does not erode photoresist such as AZ-1350 and gives high quality surfaces. The etching rate can easily be controlled by changing the etchant component proportions. Etching profiles were examined by cleaving the wafer in orthogonal directions along the (110) and ($\bar{1}$10) planes.

2. Experimental procedure

Etching studies were performed on undoped GaAs and InP wafers of (001) surface orientation with an uncertainty of 1° or less. These wafers were mechanically lapped using 0.05 μm abrasive alumina and chemically polished to a mirror-like finish in a solution of Br_2 in methanol. The etching solution was prepared by mixing $K_2Cr_2O_7$ aqueous solution, 36N H_2SO_4 and 12N HCl. A large solution quantity was prepared to prevent the etching temperature from rising and the etching solution composition from varying during the experiments. Etching was carried out in a temperature regulated water vessel at room temperature (25° C) or at a higher temperature (60° C) without illumination. The solution was freshly mixed prior to each experiment. Etching experiments were usually done by stirring by hand. The etching rate was measured from a step height between etched and unetched surfaces using a calibrated optical microscope, where half of the sample surface was coated by SiO_2 film to

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prevent chemical reaction. Etching profiles were obtained through 30 μm wide open windows defined by a common photolithography technique and were examined by cleaving the wafers in the two orthogonal [1 1 0] and [$\bar{1}$ 1 0] directions. The etched surface quality was also examined by comparison with those obtained from commonly employed etchants, such as H_2SO_4–H_2O_2–H_2O and Br_2–CH_3OH, through a specially designed SiO_2 mask pattern.

3. Results and discussion

3.1. Etching rate

Etched depth as a function of time for (0 0 1) GaAs in a solution of 3(1M $K_2Cr_2O_7$):1H_2SO_4: 2HCl by volume ratio at room temperature is shown in Fig. 1. The filled circles were obtained with stirring and the open circles without stirring. The etched depth was found to have a linear dependence on etching time. This is probably due to a chemical reaction rate limited dissolution process [1]. Etching rates were about 2.5 μm min^{-1} for the stirred condition, and 1.7 μm min^{-1} for the non-stirred condition.

Changes in etching conditions, such as temperature, as well as variations in the relative proportion of etchant components, affected etching rates. The etching rate with stirring at 60° C was 20 μm min^{-1}, which was about eight times faster than that at 25° C. Etching rate increased with increasing HCl proportion at a constant ratio of 1M $K_2Cr_2O_7$ and H_2SO_4 (i.e. 3 parts 1M $K_2Cr_2O_7$ and 1 part H_2SO_4) without any change in surface quality. The etching rates obtained are summarized in Table I along with the etchant component proportion and etching temperature. The quality of the GaAs etched surface decreases with decrease of the proportion of 1M $K_2Cr_2O_7$ aqueous solution and/or molar concentration of $K_2Cr_2O_7$. The highest quality surface was obtained with a solution of 3 parts 1M $K_2Cr_2O_7$, 1 part H_2SO_4, and an addition of HCl. Without any addition of HCl, the system acts as a slow etching rate etchant for GaAs.

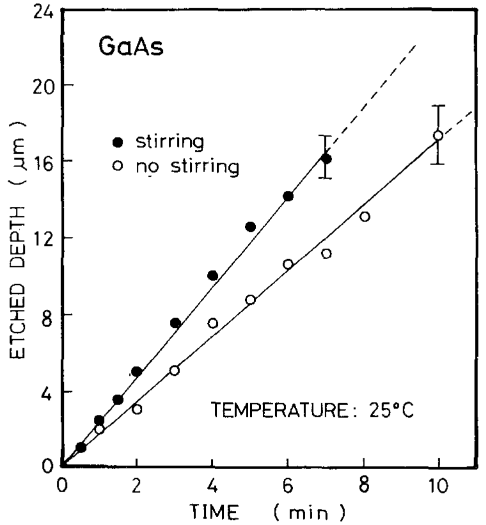

Figure 1 Relation between etched depth and etching time for GaAs in a solution of 3(1M $K_2Cr_2O_7$):1H_2SO_4: 2HCl at 25 ° C.

Etched depth as a function of time for (0 0 1) InP in the solution 3(1M $K_2Cr_2O_7$):1H_2SO_4: 2HCl at 60° C is shown in Fig. 2. The filled circles were obtained with stirring and the open circles without stirring. Etched depth was found to have a linear dependence on etching time, similar to that for GaAs. Etching rates were about 1.5 μm min^{-1} for the stirred condition and 0.5 μm min^{-1} for the non-stirred condition. The stirring effect for InP was found to be large when compared with that for GaAs. Quantitative features of this etchant system for InP were found to be essentially the same for GaAs. Without any addition of HCl, the system does not etch the InP wafer.

3.2. Etched surface quality

A comparison of surface quality for the $K_2Cr_2O_7$–H_2SO_4–HCl etchant, and for commonly used etchants, was made by making (0 0 1) GaAs with sputtered SiO_2 and defining a numerical "eight-line" and "circle" pattern with AZ-1350. The results of this experiment are shown in Fig. 3.

TABLE I Etching rates for (0 0 1) GaAs and (0 0 1) InP in a solution of α(1M $K_2Cr_2O_7$):βH_2SO_4:γHCl system

Material	Etchant α β γ	Temperature (° C)	Etching rate (μm min^{-1})
(0 0 1) GaAs	3 : 1	60	0.03
	3 : 1 : 1	60	12
	3 : 1 : 2	25	2.5
	3 : 1 : 2	25	1.7*
	3 : 1 : 2	60	20
	3 : 1 : 3	60	30
(0 0 1) InP	3 : 1	60	No etch
	3 : 1 : 1	60	0.25
	3 : 1 : 2	25	0.5
	3 : 1 : 2	60	1.5
	3 : 1 : 2	60	0.5*
	3 : 1 : 3	60	2.3

* Non-stirring condition.

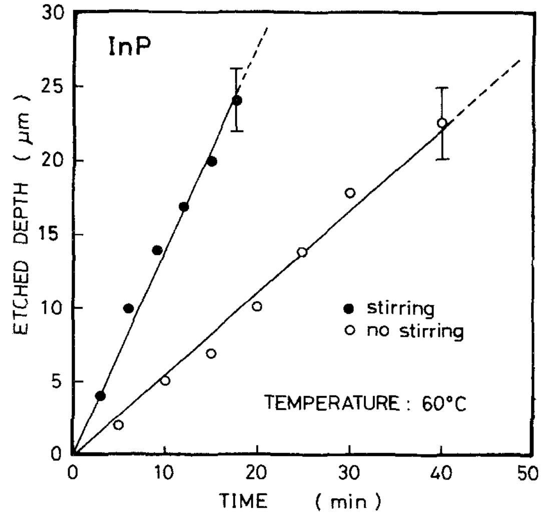

Figure 2 Relation between etched depth and etching time for InP in a solution of $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}2HCl$ at 60° C.

The solutions for each case shown were: (a) 0.3 vol% $Br_2{:}CH_3OH$; (b) $1(1\text{M}\ NaOH){:}1H_2O_2{:}10H_2O$; (c) $3H_2SO_4{:}1H_2O_2{:}1H_2O$; and (d) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}2HCl$. The $Br_2{:}CH_3OH$, $NaOH{:}H_2O_2{:}H_2O$ and $H_2SO_4{:}H_2O_2{:}H_2O$ systems are known to be the most commonly employed etchants for GaAs [1]. The samples were etched with each etchant, for a time, to provide step heights of 2 to 5 μm between etched and unetched surfaces.

As may be clearly seen in Fig. 3b, the $NaOH{:}H_2O_2{:}H_2O$ produces a broom-sweeped appearance on the etched surface. The $H_2SO_4{:}H_2O_2{:}H_2O$ (Fig. 3c) also produces a microscopic roughness, due to the production of many elliptical etch pits in the surface. The $Br_2{:}CH_3OH$ (Fig. 3a) and $K_2Cr_2O_7{:}H_2SO_4{:}HCl$ (Fig. 3d) give rise to undercutting in the direction along the $[\bar{1}10]$ crystallographic axis. These systems, however, provide etch pit free and high quality surfaces. Note that the $Br_2{:}CH_3OH$ erodes photoresists such as AZ-1350, but the $K_2Cr_2O_7{:}H_2SO_4{:}HCl$ does not perceptibly do so. The $Br_2{:}CH_3OH$ system gives etching profiles with V-shaped and reverse mesa-shaped structures for channels aligned along the $[\bar{1}10]$ and $[110]$ directions, respectively, as defined predominantly by the $(\bar{1}\bar{1}1)$ Ga slow etching rate planes [6].

Surface quality for (001) InP etched with (a) $3H_2SO_4{:}1H_2O_2{:}1H_2O$ and (b) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}1HCl$ is demonstrated in Fig. 4. The wafers were etched with each etchant, for a time, to give step heights of 2 to 4 μm between etched and unetched surfaces. The $H_2SO_4{:}H_2O_2{:}H_2O$ system produces many elliptical etch pits on the etched bottom (see, expanded photograph of each etch pit, Fig. 4a-3), similar to GaAs. As a result surface quality is thought to be not so good. If one were to use this system as an etchant for InP or GaAs, this characteristic might interrupt the fabrication of microelectronic devices. The degree of undercutting for this system is also very large and anisotropic, particularly in the direction of the $[\bar{1}10]$ crystallographic axis (compare Fig. 4a-2 with Fig. 4b-2). The $K_2Cr_2O_7{:}H_2SO_4{:}HCl$ system, on the other hand, provides etch pit free and good quality surfaces. Moreover, the undercutting for this etchant is isotropic, i.e. it occurs along all the crystallographic directions lying in the (001) plane.

3.3. Etching profile

Etching profiles for (001) GaAs etched with solutions having the following etchant component proportions are shown in Fig. 5: (a) $1H_2SO_4{:}1H_2O_2{:}1H_2O$ (25° C, 30 sec); (b) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4$ (60° C, 20 min); (c) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}1HCl$ (60° C, 1 min); (d) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}2HCl$ (60° C, 1 min); (e) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}3HCl$ (60° C, 30 sec); and (f) $3(1\text{M}\ K_2Cr_2O_7){:}1H_2SO_4{:}2HCl$ (25° C, 2 min). These profiles were obtained by cleaving the wafers in orthogonal directions along the (110) and $(\bar{1}10)$ planes. It is clear from this figure that the profile shape changes with a crystallographic rotation of 90° about the [001] axis. Such a feature clearly suggests the non-equivalence of the [110] and $[\bar{1}10]$ type directions lying in the (001) plane of zinc-blende type crystal [7].

The $H_2SO_4{:}H_2O_2{:}H_2O$ system for the (110) cleavage plane (Fig. 5a) provides etch revealed walls which are composed of two individual reverse mesa-shaped and mesa-shaped planes. The reverse mesa-shaped and mesa-shaped planes form angles of 114° and 55° with respect to the (001) surface plane and can be identified within the accuracies of the experiment as the $\{221\}$ (or $\{1\bar{1}\bar{1}\}$ Ga), and $\{\bar{1}11\}$ Ga planes, respectively. The $\{2\bar{2}\bar{1}\}$ ($\{1\bar{1}\bar{1}\}$ Ga) and $\{\bar{1}11\}$ Ga planes in principle form angles of 109.5° (125.3°) and 54.7° with respect to the (001) plane. This system gives a mesa-shaped profile for the $(\bar{1}10)$ cleavage plane, forming an angle of 55° with respect to the (001)

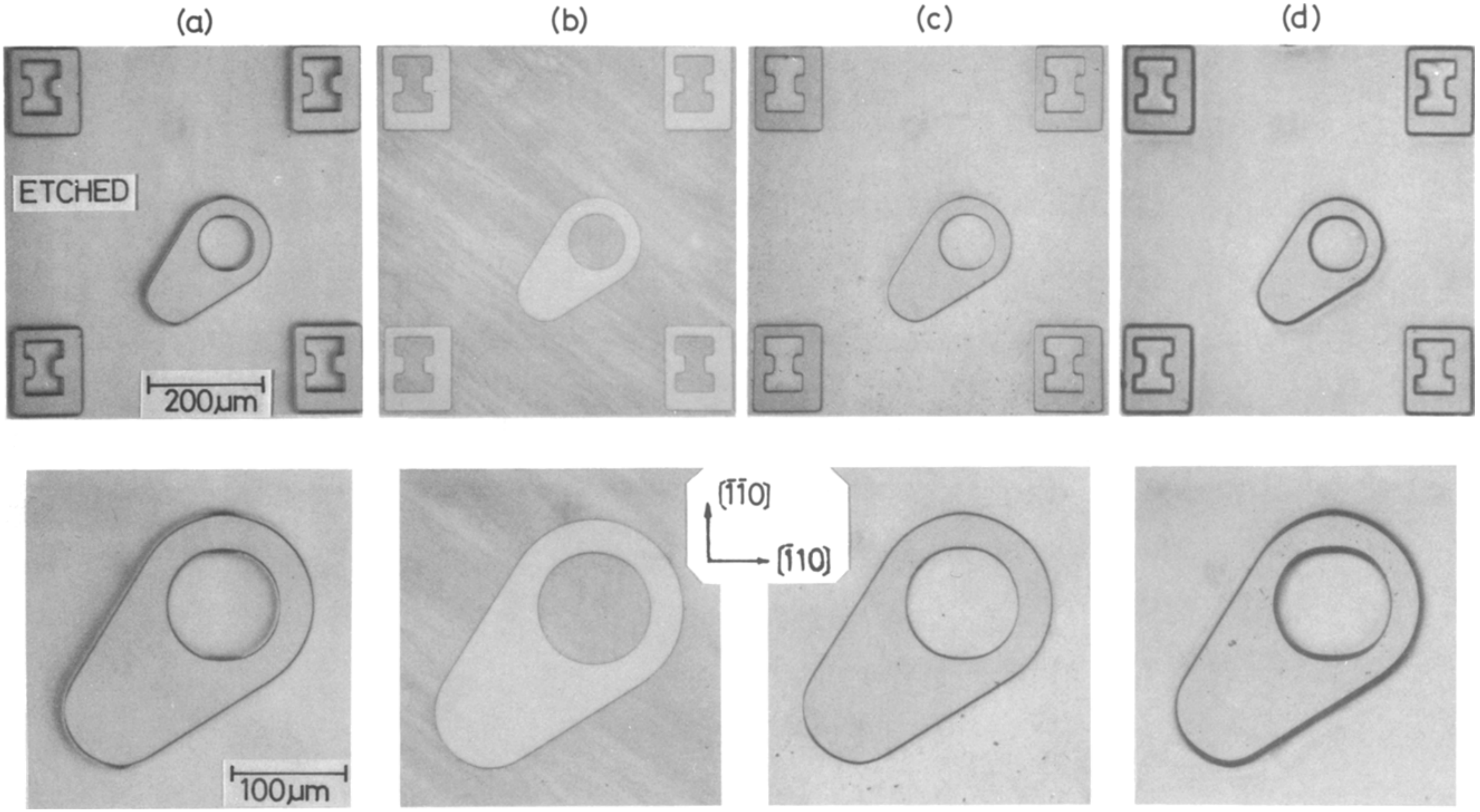

Figure 3 Surface quality comparison of (001) GaAs etched with (a) 0.3 vol% Br_2:CH_3OH, (b) 1(1M NaOH):$1H_2O_2$:$10H_2O$, (c) $3H_2SO_4$:$1H_2O_2$:$1H_2O$ and (d) 3(1M $K_2Cr_2O_7$): $1H_2SO_4$:2HCl.

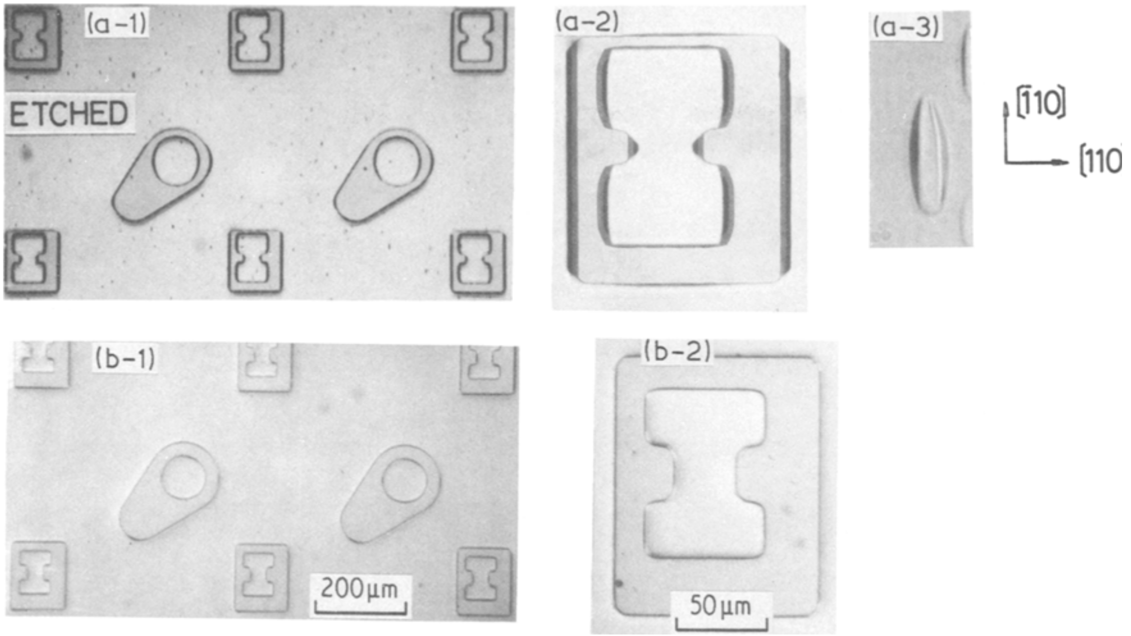

Figure 4 Comparison of surface quality for (001) InP etched with (a) $3H_2SO_4:1H_2O_2:1H_2O$ and (b) 3(1M $K_2Cr_2O_7$): $1H_2SO_4:1HCl$.

surface plane. The mesa-shaped plane corresponds to the $\{\bar{1}\bar{1}1\}$ Ga slow etching plane, where the $\{\bar{1}\bar{1}1\}$ plane forms an angle of 54.7° with respect to the (001) plane. The 3(1M $K_2Cr_2O_7$):$1H_2SO_4$ etchant (Fig. 5b) provides mesa-shaped profiles for both the (110) and $(\bar{1}10)$ cleavage planes forming an angle of 55° with respect to the (001) surface plane.

Etching profiles for the $K_2Cr_2O_7:H_2SO_4:HCl$ system are demonstrated in Fig. 5c to f. In the case of the (110) cleavage planes, the profiles indicate the vertically etched planes having a slow tilt angle from a direction normal to the (001) surface plane. These etch revealed planes are thought to correspond to the $\{\bar{1}10\}$ crystallographic planes. It is clear from the figure that the degree of undercutting for the direction along the $[\bar{1}10]$ axis is larger than for the direction along the [110] axis. (Note that the etch channel widths are defined to be 30 µm).

Fabrication of double heterostructure lasers, which incorporate chemically etched mirrors, has been reported to realize the monolithic fabrication of integrated optical devices [8,9]. Much attention has been paid in such works to produce a smooth mirror Fabry–Perot resonator by chemical etching. It is important to produce vertical etch revealed planes for the fabrication of etched mirror lasers, since the mirror reflectivity is greater for the vertical mirror than for the tapered mirror [8]. Employing the $K_2Cr_2O_7:H_2SO_4:HCl$ solution as an etchant, one can fabricate such vertical etched mirror lasers in the GaAs/GaAlAs system aligned with the mirror resonator direction along the $[\bar{1}10]$ axis.

Etching profiles for (001) InP etched with solutions having the following etchant component proportions are shown in Fig. 6: (a) $1H_2SO_4:1H_2O_2:1H_2O$(60° C, 20 min);(b) 3(1M $K_2Cr_2O_7$):$1H_2SO_4:1HCl$(60° C, 20 min);(c) 3(1M $K_2Cr_2O_7$):$1H_2SO_4:2HCl$(60° C, 20 min);(d) 3(1M $K_2Cr_2O_7$):$1H_2SO_4:3HCl$ (60° C, 20 min); and (e) 3(1M $K_2Cr_2O_7$):$1H_2SO_4:2HCl$ (25° C, 20 min). In the $H_2SO_4:H_2O_2:H_2O$ system (Fig. 6a), the profile for the (110) cleavage plane reveals etched walls almost perpendicular to the (001) surface plane defined by the $\{\bar{1}10\}$ planes, while the $(\bar{1}10)$ cleavage plane reveals a mesa-shaped structure defined by the $\{\bar{1}\bar{1}1\}$ In slow etching plane. The $K_2Cr_2O_7:H_2SO_4:HCl$ system (Fig. 6b to e) provides mesa-shaped profiles for both the (110) and $(\bar{1}10)$ cleavage planes. This characteristic etching suggests its applicability to the fabrication of most mesa-structure InP devices such as transistors and photodiodes.

Etching characteristics of cleaved $(1\bar{1}0)$ surface for an (001)-oriented InGaAsP/InP wafer etched with the 3(1M $K_2Cr_2O_7$):$1H_2SO_4:2HCl$

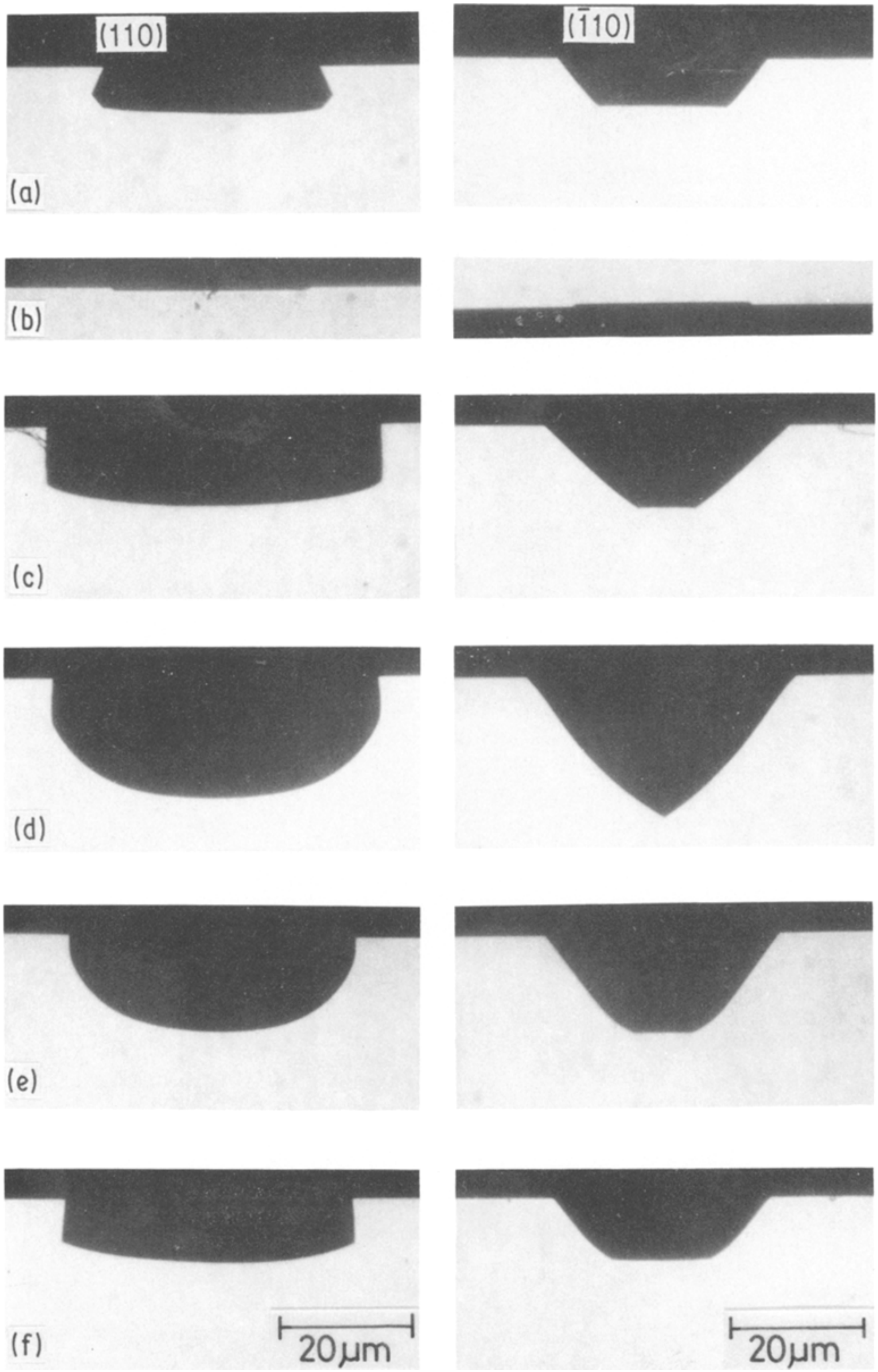

Figure 5 Etching profiles for (001) GaAs etched in solutions with various etchant component proportions: (a) $1H_2SO_4$: $1H_2O_2$: $1H_2O$ (25° C, 30 sec); (b) 3(1M $K_2Cr_2O_7$):$1H_2SO_4$ (60° C, 20 min); (c) 3(1M $K_2Cr_2O_7$):$1H_2SO_4$:1HCl (60° C, 1 min); (d) 3(1M $K_2Cr_2O_7$):$1H_2SO_4$:2HCl (60° C, 1 min); (e) 3(1M $K_2Cr_2O_7$):$1H_2SO_4$:3HCl (60° C, 30 sec); and (f) 3(1M $K_2Cr_2O_7$):$1H_2SO_4$:2HCl (25° C, 2 min).

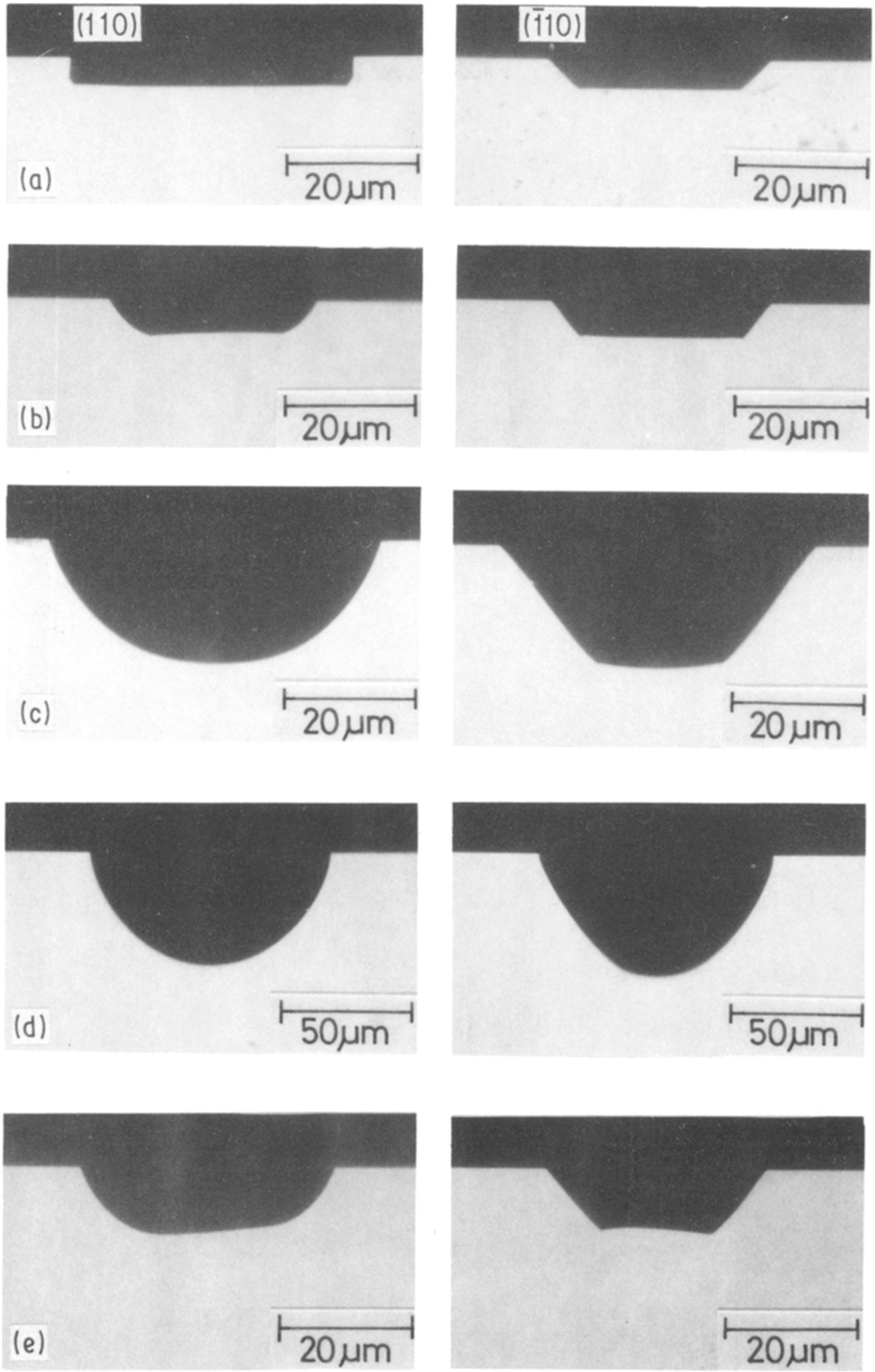

Figure 6 Etching profiles for (001) InP in solutions with various etchant component proportions; (a) $1H_2SO_4:1H_2O_2:1H_2O$ (60° C, 20 min); (b) $3(1\text{M}\ K_2Cr_2O_7):1H_2SO_4:1HCl$ (60° C, 20 min); (c) $3(1\text{M}\ K_2Cr_2O_7):1H_2SO_4:2HCl$ 60° C, 20 min); (d) $3(1\text{M}\ K_2Cr_2O_7):1H_2SO_4:3HCl$ (60° C, 20 min); and (e) $3(1\text{M}\ K_2Cr_2O_7):1H_2SO_4:2HCl$ (25° C, 20 min).

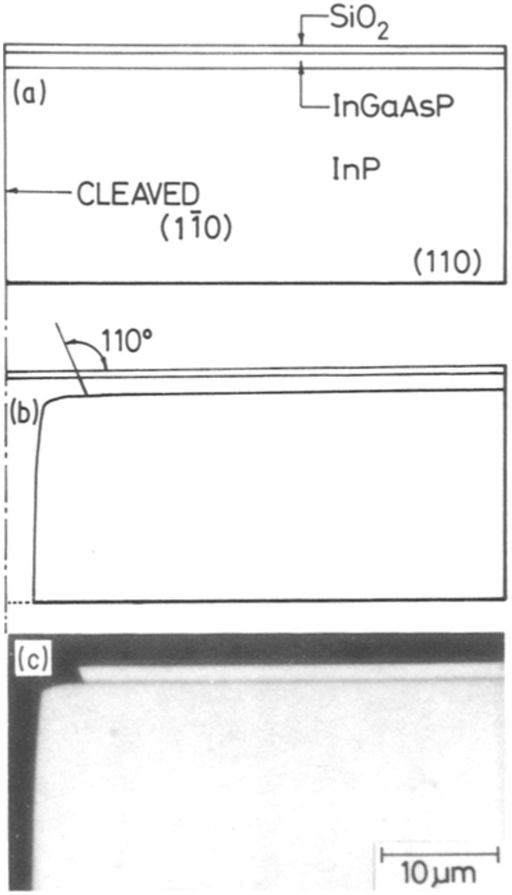

Figure 7 Etching characteristics of the $(1\bar{1}0)$ surface for an (001)-oriented InGaAsP/InP heterostructure wafer etched with 3(1M $K_2Cr_2O_7$):1H_2SO_4:2HCl (25° C, 2 min): (a) before etching; (b) after etching; and (c) photograph of the etched wafer.

(25° C, 2 min) are shown in Fig. 7. The InP was etched flatly, while the InGaAsP layer revealed an inclined plane forming an angle of 110° with respect to the [001] direction, indicating that the inclined plane could be the $(2\bar{2}\bar{1})$ crystallographic plane. The solution and heterolayer InGaAsP/InP junctions can now be expected to provide many applications for device structure design and fabrication. With InGaAsP/InP multilayer wafer, the active region was narrowed through undercutting the InGaAsP layer, which was sandwiched between the top InP layer and the active InP layer. This structure has the advantage of a large contact area combined with a narrow active region. Contact and thermal resistances are expected to be superior to those for a classical mesa structure [10]. Mesa-structure shape, of course, changes by changing the etchant component proportion, since the ratio of etching rate *R*(InGaAsP)/*R*(InP) is a function of it. The system is, thus, thought to be attractive for a variety of InGaAsP/InP device applications.

4. Conclusions

A new etching solution composed of $K_2Cr_2O_7$ aqueous solution, H_2SO_4, and HCl has been developed for etching of GaAs and InP. This etchant system provides high quality etched surfaces without any undesirable roughness or etch pits. The etching rate can be easily controlled by changing the etchant component proportions. This is especially so for the HCl proportion, and leads to no change in surface quality. Etching profiles have been examined by cleaving the wafers in orthogonal directions along the (110) and $(\bar{1}10)$ planes. Vertical wall and mesa-shaped structures have been formed on etching profiles of (001) GaAs by stripes parallel to the [110] and $[\bar{1}10]$ directions, respectively. The mesa-shaped profiles have been formed for (001) InP in both the [110] and $[\bar{1}10]$ directions. The solution does not erode photoresists such as AZ-1350 and is thereby attractive for a variety of device applications.

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