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Cite as: Appl. Phys. Lett. **37**, 1022 (1980); <https://doi.org/10.1063/1.91750>  
Published Online: 23 July 2008

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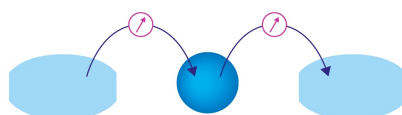
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# Reactive-ion etching of GaAs and InP using $\text{CCl}_2\text{F}_2/\text{Ar}/\text{O}_2$

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(Received 6 June 1980; accepted for publication 1 October 1980)

We describe the reactive ion etching of GaAs, InP, and their derivative compounds using an etch gas composed of  $\text{CCl}_2\text{F}_2$ ,  $\text{O}_2$ , and argon. Etching was generally carried out at pressures between 1 and  $10\mu$ , and power densities below  $0.8\text{ W/cm}^2$ . Clean etch profiles were obtained with etch rates as high as  $0.25\mu\text{m/min}$ . A strong dependence of etch rate on pressure was observed with a maximum at  $5\mu$  total pressure. The etch profiles exhibited a "negative undercut" character which was also dependent upon the total pressure.

PACS numbers: 79.20.Nc, 81.60.Dq, 41.80.Gg, 52.40.Hf

Increasing sophistication in the high-resolution transcription of submicron features utilizing UV, electron beam, or x-ray lithography demands the concomitant development of pattern transfer techniques that will preserve that resolution. Reactive ion etching, which has been increasingly utilized on silicon and silicon compounds,<sup>1</sup> is such a technique. We have successfully applied this technique to GaAs, InP, and their derivative ternary and quaternary compounds. The gas used is a mixture of  $\text{CCl}_2\text{F}_2$ , argon, and oxygen.<sup>2</sup>

The apparatus used in this study is a conventional diffusion-pumped sputtering station with a Pyrex bell jar and 12.7-cm-diam cathode and anode plates. The station was operated at 13.56 MHz. The rf matching network on the sputtering system was tuned to supply power to the bottom electrode on which the samples were etched. To minimize redeposition of sputtered material during etching, the rf-driven electrode was covered with a silicon wafer which was well heat sunk to the water-cooled electrode. The other electrode was fused quartz. A capacitance manometer was used to monitor the pressure, and the flow rates of the gases were measured using thermal mass flow meters. The gases were mixed in an external, heated manifold before entering the systems chamber. A feedback controller was used to regulate the total pressure and the flow rates for the three gases.

The successful application of the reactive ion etching technique to the III-V compounds requires the use of an etch gas which forms volatile compounds with the substrate material. Fluorine will only form volatile compounds with As and P, but the chlorides of In, Ga, As, and P are all volatile.  $\text{CCl}_2\text{F}_2$  was chosen as a chlorine-containing gas which is easy to handle and non toxic. The addition of oxygen to a halocarbon discharge can enhance the etch rate by increasing the amount of reactive species in the plasma.<sup>3</sup> For example, silicon etch rates can be several times faster in  $\text{CF}_4\text{-O}_2$  than in  $\text{CF}_4$  alone because of the increase in free F induced by the  $\text{O}_2$ . We believe that the increased etch rates observed with the addition of oxygen to  $\text{CCl}_2\text{F}_2$  can be similarly explained by an increase in free Cl species, as has been observed in the mass spectroscopy of a  $\text{CCl}_2\text{F}_2\text{-O}_2$  discharge at a few hundred microns pressure.<sup>4</sup> The argon, as well as the  $\text{O}_2$ , enhances the etch rate, perhaps by promoting surface chemical reactions and desorption of reacted products from the surface.<sup>5</sup> The argon can also sputter off small amounts of

impurities and nonvolatile products. Further, the presence of a buffer gas such as helium or argon can aid in achieving a stable plasma,<sup>6</sup> although in this case the presence of the oxygen serves a similar purpose.

Owing to the high etch rate of organic resists under these conditions, it is not possible to obtain deeply etched features ( $> 2\mu\text{m}$ ) using a layer of resist thin enough to maintain high resolution. Thus metal film masks were used which were patterned using lift-off with optical or *e*-beam lithography. Ni(Cr) was usually chosen as the mask material, although Al, Mg, Cr, and Ti were also tried, with less satisfactory results. Ni(Cr) has a small grain size<sup>7</sup> and an etch rate low enough to make it useful as a mask, without being so low that roughness in the substrate is produced from redeposition of sputtered mask material.<sup>8</sup> About 5 nm of Cr was evaporated prior to the application of the Ni(Cr) film, to assure good adhesion. Masks about 60 nm thick were formed by evaporating a small charge of Ni(Cr) to completion in a tungsten boat. To reduce strain in the film, and to obtain uniform film composition, multiple Ni(Cr) evaporations were used to form thicker masks. At no time were the substrate crystallographic axes oriented in any particular direction with respect to features on the mask.

Figure 1 is an etched GaAs sample which was patterned using *e*-beam lithography.<sup>9</sup> It was etched in a gas composed of Ar,  $\text{CCl}_2\text{F}_2$ , and  $\text{O}_2$  with relative gas flow rates in the ratio 1.0:0.1:0.1. The total flow was 20 sccm at  $10\mu$  pressure. The applied power density was  $0.5\text{ W/cm}^2$ , and the self-bias was 650 V. The width of 100 nm at the top represents the width of the original metal mask; some of the original masking material remains. The etched profile displays a "negative undercut": the profile slopes away from the mask edge rather than cutting under it, as would be true in either wet chemical etching or plasma etching. For a particular gas composition, the slope of the "overcut" appears to be a function of total pressure. More nearly vertical walls are obtained by etching at lower pressures. There is a stronger dependence of profile angle on pressure for InP than for GaAs. The slope of the overcut may result from some equilibrium rate of redeposition or adsorption on the etched walls in competition with sputtering or desorption. This overcut phenomenon has also been observed for the  $\text{CF}_4$  plasma etching of silicon.<sup>10</sup>



FIG. 1. Etched GaAs sample with a Ni(Cr) mask patterned using *e*-beam lithography. The top of the etched pedestal is the same width as the original mask. The gas composition was Ar:CCl<sub>2</sub>F<sub>2</sub>:O<sub>2</sub> with relative flow rates in the ratio of 1.0:0.1:0.1 at 10  $\mu$  pressure, 0.5 W/cm<sup>2</sup> power density, and 650 V self-bias.

The subsequent data presented in this letter were taken for a gas composition of Ar:CCl<sub>2</sub>F<sub>2</sub>:O<sub>2</sub> 1.0:1.0:1.0 (relative flow rates) and an applied power density of 0.5 W/cm<sup>2</sup>. Below 5  $\mu$  pressure, the total flow was determined by the diffusion pump speed. Above 5  $\mu$ , a throttle valve was used to keep the total flow constant at a value of 10 sccm (standard cubic centimeters per minute). We have found that these conditions produce etch rates of a few hundred nm/min for the range of total pressure from 2 to 10  $\mu$ . The surfaces of the etched substrates appear clean and smooth.

Figure 2 shows the etch rates of GaAs and InP as functions of total gas pressure. The rate increases approximately linearly with pressure below 5  $\mu$  and decreases rapidly for pressure above this value. Though this effect is not yet understood, the details of such behavior may be largely determined by the particular geometry of the etch station. For

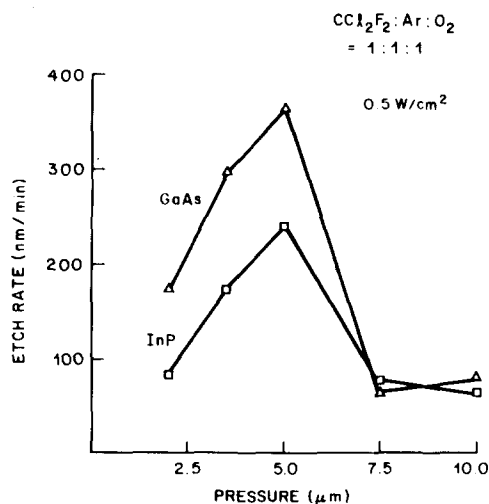


FIG. 2. Plot of etch rate vs pressure for GaAs and InP for pressure between 2 and 10  $\mu$ . The gas composition was Ar:CCl<sub>2</sub>F<sub>2</sub>:O<sub>2</sub> with relative flow rates in the ratio of 1.0:1.0:1.0 at an applied power density of 0.5 W/cm<sup>2</sup>.

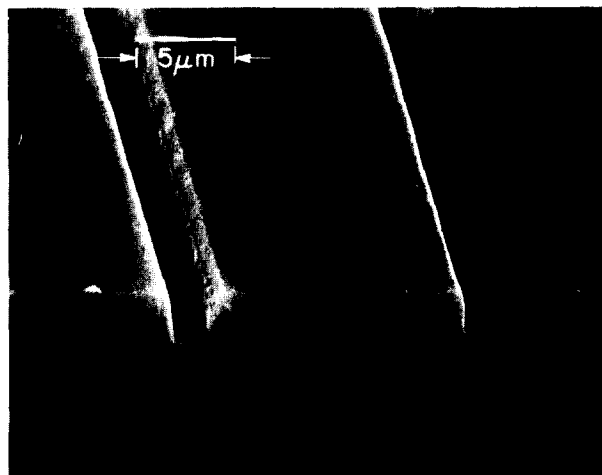


FIG. 3. SEM photograph of GaAs etched in Ar:CCl<sub>2</sub>F<sub>2</sub>:O<sub>2</sub> with relative flow rates in the ratio of 1.0:1.0:1.0 at 5  $\mu$  total pressure, 0.5 W/cm<sup>2</sup> applied power, and 550 V self-bias.

example, placing a grounded screen in the space below the cathode appears to change the shape of the curve shown in Fig. 2 by reducing the steepness of the drop in etch rate at 5  $\mu$ .

Figures 3 and 4 are scanning electron microscope (SEM) photographs of GaAs and InP, respectively, etched at 5  $\mu$  total pressure, with a self-bias of 550 V. The pedestals in the InP and the grooves in the GaAs are well delineated; the floors of the substrates are clean and fairly smooth. The total etched depth is greater than 2  $\mu$ m, using a Ni(Cr) mask 160 nm thick.

Because reactive ion etching is a high-resolution pattern-transfer technique, it should prove useful in the fabrication of high-speed electronic elements, such as field-effect transistors, and of optical gratings for use in, e.g., couplers or distributed feedback lasers. The degree of control possible over the etched wall profile suggests utility in the fabrication of laser mirrors and channel waveguides, although a better understanding of the negative undercut profile is important.

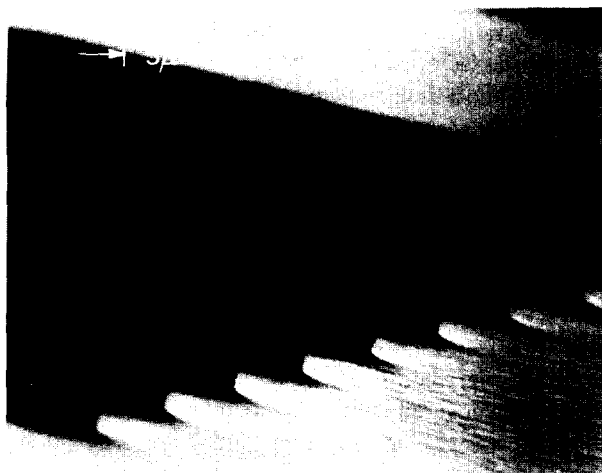


FIG. 4. SEM photograph of InP etched in Ar:CCl<sub>2</sub>F<sub>2</sub>:O<sub>2</sub> with relative flow rates in the ratio of 1.0:1.0:1.0 at 5  $\mu$  total pressure, 0.5 W/cm<sup>2</sup> applied power, and 550 V self-bias.

Moreover, because of the observed lack of selectivity of this etch process to particular crystallographic planes, device design is not constrained by substrate orientation.

We are grateful to W. A. Bonner, J. C. De Winter, and B. I. Miller for providing us with some of the substrates used in this study.

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## Heteroepitaxy of $\text{Ge}_{1-x}\text{Si}_x$ on Si by transient heating of Ge-coated Si substrates

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(Received 31 July 1980; accepted for publication 30 September 1980)

Heteroepitaxial films of  $\text{Ge}_{1-x}\text{Si}_x$  alloys have been obtained by transient heating of Ge-coated Si single-crystal substrates with a graphite strip heater. Structural characterization shows the films to be of good epitaxial quality. As the maximum temperature during heating is increased, the Ge content and the microtwin density of the films decrease.

PACS numbers: 81.30. - t, 68.55. + b, 81.40. - z, 84.60. - h

This letter describes the formation of heteroepitaxial  $\text{Ge}_{1-x}\text{Si}_x$  alloy films by transient heating of Ge-coated Si single-crystal substrates. The results of preliminary experiments indicate that it should be possible to grow high-quality GaAs epi-layers on such  $\text{Ge}_{1-x}\text{Si}_x$  films by chemical vapor deposition (CVD), thereby permitting Si substrates to be used in the production of efficient, low-cost GaAs solar cells.

We recently reported<sup>1,2</sup> the fabrication of high-performance GaAs solar cells (with efficiencies over 20% at AM1) that utilize GaAs epi-layers only  $4\text{ }\mu\text{m}$  thick grown by CVD on single-crystal Ge substrates. If such thin-film GaAs cells could be fabricated on Si substrates, they could be produced at much lower cost than conventional GaAs cells. However, attempts to prepare high-quality GaAs films by CVD growth directly on Si substrates have not been successful, primarily because the lattice constant of Si is about 4% smaller than that of GaAs, whereas Ge is closely lattice matched to GaAs.

A possible solution to the problem of GaAs/Si lattice mismatch is suggested<sup>1,3</sup> by the fact that Si and Ge are completely miscible in the solid state, forming alloys whose lattice constants vary continuously with composition. If a Si substrate were covered with a heteroepitaxial  $\text{Ge}_{1-x}\text{Si}_x$  alloy film that was graded in composition from Si rich at the substrate interface to Ge rich at the front surface, the stress due to lattice mismatch might be relieved sufficiently to permit a GaAs epi-layer of satisfactory crystal quality to be grown on the film. In this investigation we have studied the

formation of heteroepitaxial  $\text{Ge}_{1-x}\text{Si}_x$  films by transient heating of Ge-coated Si substrates with a graphite strip heater. In earlier investigations, heteroepitaxial Ge films on Si have been obtained by pulsed electron beam<sup>4</sup> or laser<sup>5,6</sup> heating of such substrates, but these films were found to contain rather high concentrations of crystal defects.

To prepare samples for transient heating, electron beam evaporation or rf sputtering was used to deposit a Ge or Ge/Si film about  $0.25\text{ }\mu\text{m}$  thick on the polished surface of commercial (100) Si wafers. The wafers were cleaned by conventional procedures and rinsed with dilute HF just before loading into the deposition system. The *e*-beam system was evacuated with an oil-diffusion pump, the sputtering system with a turbomolecular pump. Films of Ge could be deposited in either system, Ge/Si films only by sputtering. The as-deposited films were amorphous; the concentration of oxygen at the film-substrate interface was below the detection limit of Auger spectroscopy (estimated to be about 0.1%). The coated wafers were cut into individual samples with dimension of about  $0.05 \times 1 \times 2\text{ cm}$ .

The heating element of the strip heater was a graphite strip with dimensions of  $0.1 \times 6 \times 10\text{ cm}$ . The ambient was high-purity Ar. A Chromel-Alumel thermocouple (wire diameter 0.1 mm) imbedded near the center of the graphite strip was used to monitor the temperature. The sample was placed at the center of the strip, usually with the Ge-coated side facing up so that the effects of heating could be observed