Etching InP with H_2, BCl_3 and Ar

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Abstract

When hydrogen is added to a BCl_3 plasma the etch rate of InP is decreased substantially. Mass spectrometer data indicates that the chlorine only etchant ions are the dominant etching species. When hydrogen is added to the plasma, the hydrogen etchant species that are formed absorbed on the InP surface faster then the chlorine only etchant species. Therefore, the hydrogen etchant species preclude the chlorine only etchant species from being absorbed on the InP surface. As more hydrogen is added to the gas phase, more chlorine only etchant species are precluded from being absorbed on the InP surface. Since less chlorine only etchant species are available to etch the InP surface then the overall etch rate is reduced.

INTRODUCTION

Very high etch rates are needed to be able to form deep trenches and backside via holes in InP wafers. Published articles indicate that dry etching of InP with hydrogen generally does not produce high enough etch rates to be practical yet the wafer can be etched at low temperatures and the etched surface is generally smooth [1, 2, 3]. Other articles show that dry etching of InP with chlorine can produce very high etch rates but requires high wafer temperatures and the etched surface is sometimes rough [4, 5]. If hydrogen is added to the Cl_2 plasma to reduce the etch temperature and reduce the roughness of the etched surface, the etch rate of the InP is substantially decreased. Published articles suggest that the added hydrogen reacts with the chlorine in the plasma to produce HCl ions and the HCl ions etch InP at a slower rate than the chlorine ions [4, 5, 6]. An alternative to etching InP with chlorine is to etch it with BCl_3. Published articles show that BCl_3 plasmas can etch InP at comparable etch rates to chlorine plasmas [7, 8, 9], but, little is known about what happens to the etch rate when hydrogen is added. What is known is when nitrogen is added to the BCl_3 plasma the etch rate of the InP is increased. Experiments have shown that the nitrogen increases the amount of chlorine ions in the BCl_3 plasma and, therefore, the etch rate is increased [9]. If hydrogen is added to a BCl_3 plasma it may be possible to have the good qualities of hydrogen and still achieve high etch rates. Therefore, it is important to know if adding hydrogen to a BCl_3 plasma increases or decreases the etch rate of InP and why.

This paper will present data on what happens to the etch rate of InP when H_2 is added to a BCl_3 plasma. This paper will also present data from a mass spectrometer that sampled the gas phase during the etching of the InP. The mass spectrometer and the etch rate data will then be used to propose a mechanism to explain the etching of InP in a BCl_3 and H_2 plasma.

EXPERIMENTAL SETUP

A Plasma Therm SLR 770 ECR etcher was used to perform all of the etching discussed in this article. To determine the etch rate of the InP, several 4.0 cm^2 pieces of semi-insulating InP (Fe-doped) were prepared and patterned with 40 µm holes using standard photolithography techniques. All the pieces were baked at 180 °C for 90 min just prior to being etched. The etch runs held all the conditions constant except for the flow of hydrogen and argon. The etch conditions were: chuck temperature of 180 °C, BCl_3 flow of 6 sccm, argon flow of 28 to 22 sccm, hydrogen flow of 0 to 6 sccm, pressure of 6 mT, RF power of 300 watts, microwave power of 600 watts, upper magnet of 180 amps, lower magnet of 20 amps, and an etch time of 30 minutes. As the hydrogen flow was increased, the argon flow was decreased to keep the total flow constant. One InP piece at a time was placed on a 3.25 inch silicon wafer without any vacuum grease and etched using the previously mentioned etch conditions. After an etch run the piece was cross-sectioned and the etch depth was measured using a calibrated microscope.

A Hiden EQP 300 mass spectrometer was used in a positive ion collection mode to sample the gas phase during the etching of the InP. A 300 µm diameter sampling port was installed in the probe that caused approximately 2E-6 torr pressure in the mass spectrometer during the etch runs. The inlet port was set 8.0 cm from the InP piece during the etching. Before any mass spectra were obtained the mass spectrometer was tuned for maximum sensitivity on mass number 116 ($B^{11}Cl^{35}{}_3{}^+$) and the settings stayed the same throughout the rest of the investigation. Each mass spectrum that was obtained consisted of an average of five scans collecting the peak intensity of mass numbers from 1 to 300. Before starting of the etch runs a background mass spectrum was obtained using only an argon plasma (see Figure 1). This figure shows that there are no species above a mass number of 140 and the intensity of the species below this mass number is very low (except for mass number 40, which is Ar^+). Figure 2 shows a baseline mass spectrum for a BCl_3 and Ar plasma using the same etch conditions as described in the previous paragraph except with no hydrogen flowing. This figure shows a very complex spectrum and that most of the mass numbers below 140 have intensities much greater than the background counts seen in Figure 1, so subtraction of the background intensities will not be necessary. After obtaining the background and the baseline spectra (Figures 1 and 2) a 5 cm^2 InP piece with no photoresist was put in the etcher and etched using the same conditions as was used to obtain the baseline spectrum. Figure 3 shows the mass spectrum obtained while etching this InP piece. It can be seen that there is little difference between this figure and Figure 2. Since a BCl_3 plasma has a very complex spectrum and the by products of the etch process do not readily standout the following methodology was used to obtain useful mass spectra data.

First, a list was derived of the possible species that could be produced during the plasma etching of InP by H_2 and BCl_3 along with their mass numbers (see Table 1). Second, these species were then categorized into either: 1) chlorine only, no hydrogen, containing etchants (hereafter called Cl only etchants), 2) chlorine only, no hydrogen, containing by products (hereafter called Cl only by products), 3) hydrogen, and possibly chlorine, containing etchants (hereafter called H+Cl etchants), 4) hydrogen, and possibly chlorine, containing by products (hereafter called H+Cl by products), 5) by products that did not contain hydrogen or chlorine (hereafter called Other by products), and 6) mass numbers that were possibly two different species (this category was not used in the analysis of the mass spectra data). Third, mass spectra were obtained during etch runs with an InP piece that had no photoresist so that by products from the photoresist did not confused the analysis. Fourth, the intensity data from the mass spectra were separated into the different specie categories. Fifth, the intensity data for all the mass species in each category was summed together. Sixth, the trend in the intensity data for each category was compared with the etch rate data. Seventh, the trend data was also used to understand the etch rate data.

RESULTS AND DISCUSSION

Figure 4 shows that the etch rate of InP decreased substantially as the hydrogen flow increased. This figure also shows that the DC bias increased as the hydrogen flow increased. Since it would be expected that the etch rate would increase with increasing DC bias then this increase in the DC bias is not the cause of the etch rate decrease.

The trend in the intensity data for the different categories is shown in Figure 5 where it is seen that the intensity increased (when the hydrogen flow was increased) for all categories except the Cl only by products category. This indicates that by adding hydrogen to the plasma more Cl only etchants are created, more H + Cl etchants are created, more H + Cl by products are created, and more Other by products are created, but, there are less Cl only by products. For the Cl only by products category the intensity decreased when hydrogen was added to the plasma. Figure 6 compares both the etch rate and the intensity data for the Cl only by products category. It is seen in this figure that the slope of the intensity curve matches the slope of the etch rate curve. This indicates that the etch rate is dominated by the Cl only by products. Since the Cl only by products can only come from the Cl only etchants (as they etch the InP), then as hydrogen is added to the plasma the etch rate of the Cl only etchants is being reduced. Yet, when hydrogen is added to the plasma more Cl only etchants are created suggesting there should be more Cl only by products. To understand these seemingly conflicting results a discussion of the etching mechanism is necessary.

The etching of InP by H_2 and BCl_3 proceeds through several steps. The first step is the gas flow into the etcher in the area of the ECR plasma. Here the gas is ionized and reacts with other ions to form either Cl only etchants or H+Cl etchants. These ions move to the wafer surface and are absorbed. While absorbed on the surface the ions react with the InP to produce indium or phosphorus chlorides and hydrides, which are the by products of the etching. These by products then leave the wafer surface and move into the plasma where they are ionized. Eventually the by product ions move to the exhaust of the etcher. To explain the etch rate results it is assumed that the H+Cl etchants absorb upon the same sites where the Cl only etchants are absorbed and that their absorption rate is faster then the absorption rate of the Cl only etchants. By absorbing on the same site, the H+Cl etchants preclude the Cl only etchants from being absorb. As more hydrogen is added to the plasma more H+Cl etchants are produced and, thus, more are absorb on the InP surface. As more H+Cl etchants are absorbed less Cl only etchants are absorb, thus, reducing the amount of etching by the Cl only etchants and also the amount of Cl only by products. Since the etch rate is dependent upon the production of Cl only by products, when hydrogen is added to the plasma the overall etch rate is decreased. This is an explanation of why the etch rate of InP is decreased when hydrogen is added to a BCl_3 plasma.

SUMMARY

When hydrogen is added to a BCl_3 plasma the etch rate of the InP is decreased substantially. Mass spectrometer data indicates that the hydrogen reduces the etching of InP by precluding the chlorine only etchants from being absorbed on the InP surface. As more hydrogen is added to the gas phase, more chlorine only etchants are precluded from being absorbed on the InP surface. If the ions that contain hydrogen etch the InP at a slower rate (than the ions that contain only chlorine) and there are more hydrogen containing enchants absorbed on the InP surface, then the overall etch rate is reduced. This is an explanation of why adding hydrogen to a BCl_3 plasma causes the etch rate of InP to be reduced.

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TABLE 1

Mass numbers of possible ion species that could be produced during the plasma etching of InP by H_2 and BCl_3 along with their mass numbers and the category to which there were assigned (see paper).

Mass Number	Species	Category
1	H^+	3
2	H_2^+	3
3	H_3^+	3
31	P^+	5
32	PH^+	4
33	PH_2^+	4
34	PH_3^+	4
35	Cl^{35+}	1
36	HCl^{35+}	3
37	Cl^{37+}	1
38	HCl^{37+}	3
41	PB^{10+}	5
42	PB^+	5
43	HPB^+	4
46	BCl^{35+}	1
47	$BHCl^{35+}$	3
48	BCl^{37+}	1
49	$BHCl^{37+}$	3
62	P_2^+	5
63	HP_2^+	4
66	PCl^{35+}	2
67	$PHCl^{35+}$	4
68	PCl^{37+}	2
69	$PHCl^{37+}$	4
77	$PBCl^{35+}$	2
78	$PBHCl^{35+}$	4
79	$PBCl^{37+}$	2
80	$PBHCl^{37+}$	4
81	BCl_2^{35+}	1
82	$BHCl_2^{35+}$	3
83	$BCl^{35}Cl^{37+}$	1
84	$BHCl^{35}Cl^{37+}$	3
85	BCl_2^{37+}	1
86	$BHCl_2^{37+}$	3
93	P_3^+	5
94	HP_3^+	4
101	PCl_2^{35+}	2
102	$PHCl_2^{35+}$	4
103	$PCl^{35}Cl^{37+}$	2
104	$PHCl^{35}Cl^{37+}$	4
105	PCl_2^{37+}	2
106	$PHCl_2^{37+}$	4
112	$PBCl_2^{35+}$	2
113	$PBHCl_2^{35+}$	4
114	$PBCl^{35}Cl^{37+}$	2
115	$PBHCl^{35}Cl^{37+} + In^+$	6
116	$BCl_3^{35+} + PBCl_2^{37+} + InH^+$	6
117	$BHCl_3^{35+} + PBHCl_2^{37+}$	6
118	$BCl_2^{35}Cl^{37+}$	1
119	$BHCl_2^{35}Cl^{37+}$	3
120	$BCl^{35}Cl_2^{37+}$	1
121	$BHCl^{35}Cl_2^{37+}$	3
122	BCl_3^{37+}	1
123	$BHCl_3^{37+}$	3
124	P_4^+	5
125	HP_4^+	4
136	PCl_3^{35+}	2
137	$PHCl_3^{35+}$	4
138	$PCl_2^{35}Cl^{37+}$	2
139	$PHCl_2^{35}Cl^{37+}$	4
140	$PCl^{35}Cl_2^{37+}$	2
141	$PHCl^{35}Cl_2^{37+}$	4
142	PCl_3^{37+}	2
143	$PHCl_3^{37+}$	4
147	$PBCl_3^{35+}$	2
148	$PBHCl_3^{35+}$	4
149	$PBCl_2^{35}Cl^{37+}$	2
150	$InCl^{35+} + PBHCl_2^{35}Cl^{37+}$	6
151	$InHCl^{35+} + PBCl^{35}Cl_2^{37+}$	6
152	$InCl^{37+} + PBHCl^{35}Cl_2^{37+}$	6
153	$InHCl^{37+} + PBCl_3^{37+}$	6
154	$PBHCl_3^{37+}$	4
161	$InBCl^{35+}$	2
162	$InBHCl^{35+}$	4
163	$InBCl^{37+}$	2
164	$InBHCl^{37+}$	4
185	$InCl_2^{35+}$	2
186	$InHCl_2^{35+}$	4
187	$InCl^{35}Cl^{37+}$	2
188	$InHCl^{35}Cl^{37+}$	4
189	$InCl_2^{37+}$	2
190	$InHCl_2^{37+}$	4
196	$InBCl_2^{35+}$	2
197	$InBHCl_2^{35+}$	4
198	$InBCl^{35}Cl^{37+}$	2
199	$InBHCl^{35}Cl^{37+}$	4
200	$InBCl_2^{37+}$	2
201	$InBHCl_2^{37+}$	4
220	$InCl_3^{35+}$	2
221	$InHCl_3^{35+}$	4
222	$InCl_2^{35}Cl^{37+}$	2
223	$InHCl_2^{35}Cl^{37+}$	4
224	$InCl^{35}Cl_2^{37+}$	2
225	$InHCl^{35}Cl_2^{37+}$	4
226	$InCl_3^{37+}$	2
227	$InHCl_3^{37+}$	4
231	$InBCl_3^{35+}$	2
232	$InBHCl_3^{35+}$	4
233	$InBCl_2^{35}Cl^{37+}$	2
234	$InBHCl_2^{35}Cl^{37+}$	4
235	$InBCl^{35}Cl_2^{37+}$	2
236	$InBHCl^{35}Cl_2^{37+}$	4
237	$InBCl_3^{37+}$	2
238	$InBHCl_3^{37+}$	4

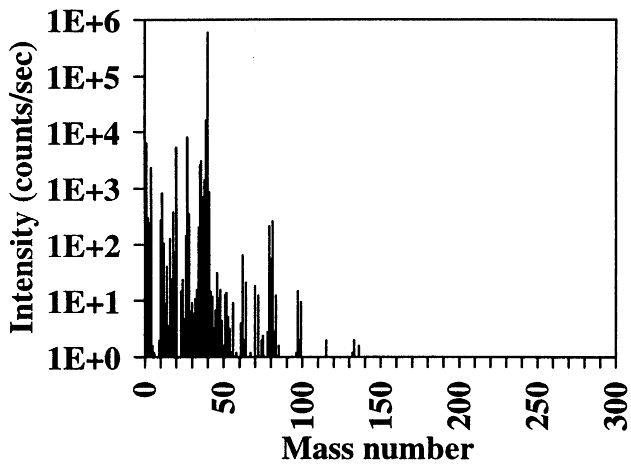

Fig. 1: Mass spectrum of an argon plasma.

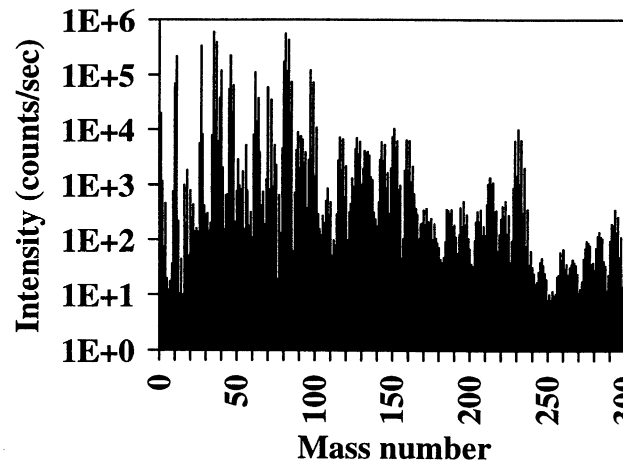

Fig. 2: Mass spectrum of a BCl_3 and argon plasma.

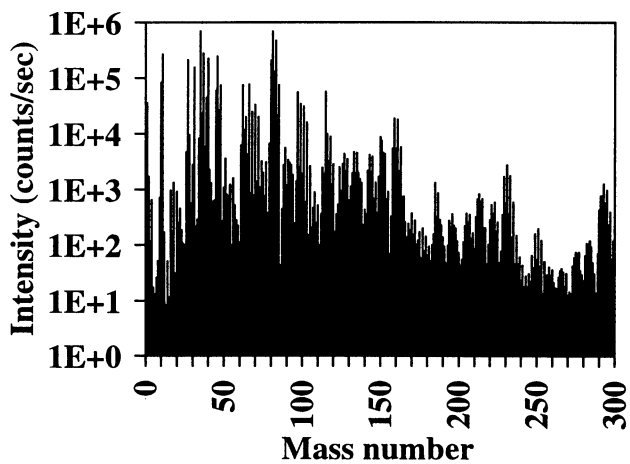

Fig. 3: Mass spectrum of BCl3 and argon plasma while etching an InP piece.

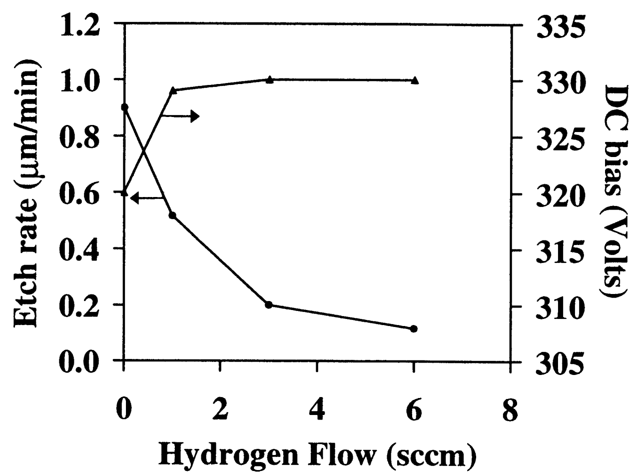

Fig. 4: The etch rate of InP in a H_2, BCl_3, and Ar plasma as a function of H_2 flow. Also the DC bias during the etching as a function of H_2 flow.

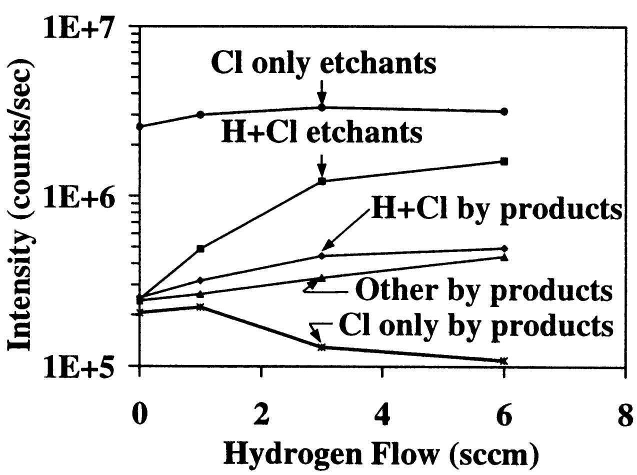

Fig. 5: Intensity for the different categories as a function of hydrogen flow (see paper and Table 1 for what species are in each category).

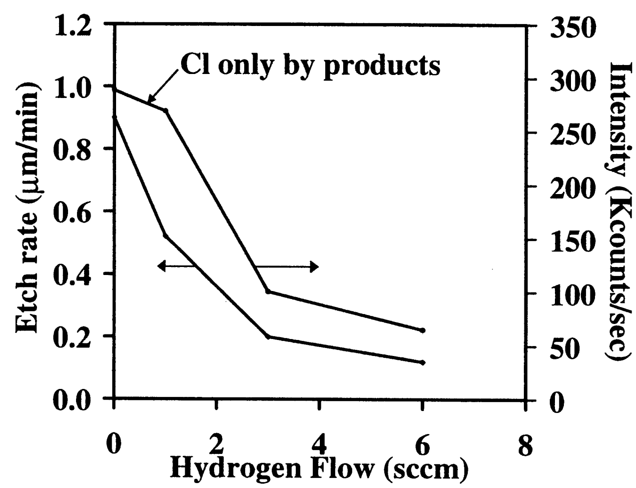

Fig. 6: The etch rate and intensity of the chlorine only by products as a function of H_2 flow.