Etching behaviour of GaAs with chlorine chemically assisted ion beam etching depending on the surface temperature

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ABSTRACT

The chemically assisted ion beam etching (CAIBE) of GaAs as well as the sputtering and the pure chemical etching (CE) at different surface temperatures and chlorine fluxes have been studied. At elevated surface temperature a noticeable increase of the etch rate compared to room temperature etching for CE and CAIBE was achieved whereas sputtering is not depending on the temperature. An etch rate of higher than 1 µm/min at an ion beam energy of 400 eV, a chlorine flux of 10 sccm Cl_2, and a temperature of 420 K could be obtained. An electronic beam chopper has been utilised in order to obtain a better insight into the kinetics of the formation and the etching process of the reaction products. A lower pulse length modulation reduces the total ion beam exposure time at the same etch depth. Hence, a lower surface damaging could be the consequence.

INTRODUCTION

Chemically assisted ion beam etching (CAIBE) of GaAs with chlorine, first studied by Geis *et al.* (1), has been extensively studied for a long time. Generally this process goes off as follows, inert gas ions are accelerated from an ion beam source to the sample surface. Additionally, a chemical reactant, usually chlorine, is fed through a nozzle which is directed to the sample surface. Complex surface processes result in the formation of more or less volatile reaction products depending on the used materials and the experimental conditions. The reaction of chlorine with GaAs proceeds stepwise from monochloride over dichloride to trichloride (2). The arsenic chloride is highly volatile at room temperature whereas gallium chloride remains at the surface without additional activation. Principally, the etching mechanism of the CAIBE process can be understood as an interaction between physical, chemical and ion-enhanced erosion effects. Two of the effects, namely physical mechanism, i.e. the impact of inert gas ions on the substrate surface also referred as sputtering, and the chemical mechanism (3), i.e. the chemical reaction between reactive gas (chlorine) molecules and substrate atoms, have been studied independently and are well understood in this context (4). However, the influence of the ion-enhanced factor on the etch behaviour is still under investigation.

Opposite to normally used ion beam etching (IBE), the independent control of the CAIBE etch parameters, e.g. chlorine flux, ion beam energy, surface temperature etc., allows the etching of structures with vertical sidewalls (5, 6), smooth surfaces, and results also in larger etch rates, a higher selectivity (7) and a lower ion beam damage. Thus, this process is very useful for the fabrication of integrated optical elements like surface gratings (5) or prisms. Nevertheless, there remain still some obscurities in the understanding of the etching process itself. The exact reaction mechanism of the reactive species with the surface atoms at industrial used parameter sets applying energetic ions is yet not fully known. Typically, a deviation of the etch rate from the expected square root dependence on the ion beam energy for a physical etching mechanism can be noted (5). Probably this is attributed to a heating of the surface due to the momentum transfer of the accelerated ions to the surface. Therefore, the influence of the surface temperature on the CAIBE process in order to obtain a better insight into the complex etching process itself and the interaction between the different etching mechanisms is investigated in this study. A better understanding of the influence of the process parameters will qualify the CAIBE process for industrial fabrication usage with an increased reliability and quality.

EXPERIMENTAL

For the investigations an UHV system with a base pressure of better than 1×10^{-8} mbar has been utilised. The experiments were carried out with an ECR (electron cyclotron resonance) ion beam source of type EC/F 125 (details to the ion source see Zeuner *et al.* (8)) . The ion current density of the argon ion beam was measured by a 4 x 4 Faraday cup array. The etching of GaAs(100) was performed at a pressure of about $0.4 - 1 \times 10^{-3}$ mbar depending on the chlorine flux directed through a nozzle to the sample surface. A special designed sample holder with helium back side coupling allows the cooling (water or liquid nitrogen) or heating (resistance heating element) of the sample in the temperature range of 200 K to 500 K. The temperature was measured with a k-type thermocouple on top of the sample holder.

An electronic beam chopper has been utilised to control the ion beam acceleration voltage while the other supply parameters of the ion source and the chlorine flux to the sample surface remain unchanged. Time resolved measurements

with an oscilloscope of the ion current from the Faraday cups were carried out. When the ion beam is switched on (ion beam exposure time) the inert gas ions will be accelerated to the sample surface. Therefore a positive current peak with a rise time of 0.05 ms was measured with the oscilloscope. This period corresponds to the normal CAIBE process. During the period without ion beam, only chlorine molecules can interact with the surface (chlorine coverage time) and form chlorides if the activation energy is high enough. The time resolved measurement revealed a negative current attributed to the emission of electrons. Due to the usage of an external pulse generator it was possible to use frequencies in the range from 100 Hz to 10 kHz with a pulse length modulation (PLM) between 0.1 and 0.9. The PLM is defined as the ratio of the ion beam exposure time to the cycle duration (summation of ion beam exposure time and chlorine coverage time).

RESULTS

It is known, that despite a water cooling of the sample holder the surface temperature increases slightly with processing time depending on the used etch parameters. Thereby, the steady state surface temperature is mainly influenced by the ion beam energy, the ion current density, the conductive heat flow from the sample surface to the cooled sample holder and the radiation from the sample surface (9). For example, in the experiments with an ion beam energy of 400 eV, an ion current density of 0.5 mA/cm^2 and a water temperature of 290 K an almost steady state surface temperature of about 390 K without and 320 K with helium back side coupling after 80 minutes processing time starting at room temperature was found. Without helium back side coupling the averaged etch rate increased nearly linear with the processing time, i.e. with the rise of the surface temperature. In contrast, no change of the etch rate could be observed in the experiments with the helium back side coupling. Applying the helium back side coupling, the increase of the surface temperature by the etch process can be avoided and therefore, reproducible and stabile etch results can be achieved. Because of the low reproducible etch results without helium back side coupling it can be concluded that the temperature has an important effect on the etching of GaAs. Thus, the influence of the surface temperature on the etch behaviour for the CAIBE process of GaAs should be investigated in detail under defined etch conditions.

The etch rate dependence on the surface temperature for selected etch methods like IBE, CE and CAIBE is shown in Figure 1. The IBE process of GaAs with argon ions reveals no substantial change of the etch rate in the studied temperature range. The chemical etching (CE), to be understood as a sequence of the adsorption of chlorine molecules, the reaction with the surface atoms and the desorption of these reaction products, was studied without argon ion beam assistance and revealed a distinct temperature dependence. In accordance with Bond *et al.* (4), it is important to remove the native oxide layer prior to the CE process. Hence, pre-sputtering of the GaAs surface in the etch chamber in order to remove the oxide layer and to guarantee the same initial conditions was used for all CE experiments. Below 300 K no erosion by the CE process could be observed. Probably, the temperature is not sufficient enough to cause the desorption of reaction products. However, at elevated surface temperatures a measurable removal can be seen. Up to 400 K the etch rate increases with the temperature and is nearly independent of the used chlorine flux. Thus the desorption of the reaction products is a rate limiting process. At temperatures above 400 K the etch rate tends to be independent of the surface temperature. This might be due to the fact that in this temperature range the etch rate starts to be limited by the chlorine flux to the substrate surface. The desorption of the reaction products is much faster than the reaction of new chlorine with GaAs at the substrate surface, i.e. the process is flux limited. Figure 2 presents an Arrhenius plot of the CE etch rate depending on the reciprocal temperature for different chlorine fluxes. A variation of the activation energy depending on the surface temperature can be observed. This indicates also a change of the rate limiting process and/or a creation of different reaction products. Su *et al.* (10) proved with modulated molecular beam scattering (MMBS) and temperature-programmed reaction (TPR) the change of the reaction products from $GaCl_3$ to GaCl at increasing surface temperature (300 K to 600 K). At temperatures below 400 K the desorption enthalpy for GaCl was determined to be 1.12 eV and for $GaCl_3$ to be 0.14 eV (4). At high chlorine fluxes and temperatures below 400 K arsenic will be desorbed from the surface as $AsCl_3$ with a desorption enthalpy much lower than that for $GaCl_3$. (11). Therefore, in the investigated temperature range the desorption of $GaCl_3$ is the rate limiting factor. Although etch conditions strongly related for practical use were applied, the determined activation energy for the etching process is in the same dimension.

Relating to Figure 1, the summation of the etch rates of both basic etch mechanisms considered above (IBE and CE) result in a value that is still lower than the experimental measured etch rate of the CAIBE process. Hence, it is clear that besides the pure physical and chemical reaction mechanism an interaction between both mechanisms exists that causes the higher etch rate. Hence, also the sputtering of reaction products or adsorbed chlorine should not be neglected as part of the CAIBE process. As seen in Figure 1 additionally, a stronger etch rate dependency of the CAIBE curves on the chlorine flux compared to the CE process alone exists. Already at room temperature a difference of the etch rates can be observed. Several assumptions exist to interpret this difference (4, 12, 13). In accordance with this, here it is supposed, that at this temperature the momentum transfer from the accelerated ions to the sample surface causes an ion-enhanced erosion. Thus, the temperature in the surface layer increases slightly but is, however, not detectable with the used thermocouple. In contrast to this, the usage of the resistance heating element caused a heating of the substrate surface whereby the CAIBE etch rate could be increased additionally. Compared to 300 K, a strong increase of the etch rate can

be achieved when the surface temperature is raised. Thus, a maximal etch rate of 1.2 µm/min was measured at a temperature of 420 K and a chlorine flux of 10 sccm. However, the decrease of the etch rate at temperatures above 420 K is still puzzling. The lack of chlorine for the chemical reaction could be responsible for this, because both, CE and CAIBE, show evidence for a chorine flux limitation (compare to Fig. 1 and 2). The most likely reason for this chlorine limitation is the change of the sticking coefficient with temperature.

In order to get a further insight into the etch mechanisms a chopped ion beam was used. This enables the study of the reaction dynamics of the reactive species at different time scales. All experiments were carried out at a constant ion beam exposure time per period of 0.1 ms, whereby the total ion beam exposure time was fixed to 200 s. Generally, a shorter PLM means a longer chlorine coverage time and hence a stronger coverage of the sample surface with chlorine and chloride, respectively, if chemical reaction takes place. In Figure 3 the etch depth depending on the PLM at different surface temperatures is shown. The increase of the etch depth at a surface temperature of 420 K with decreasing PLM seems to be influenced by the spontaneous etching (CE process) of GaAs at temperatures above 300 K. An additional thermal removal of reaction products is taking place when the ion beam power supply is switched off. However, what is the reason for the same etch behaviour at surface temperatures of 200 K and 300 K? Since a higher surface coverage proceeds with a longer PLM at a constant ion beam exposure time per pulse, more reaction products as well as high-ordered chloride will be formed and thus the removal will be enhanced if the ion beam is switched on. The difference among the two temperatures of 200 K and 300 K is probably influenced by a lower reaction rate of chlorine at lower surface temperatures. If the PLM is decreased towards Zero for temperatures above 300 K the etch depth increases further due to the additionally thermal erosion. At temperatures below 300 K the etch depth will be limited to a value resulting on the fully coverage of the sample surface with reaction products, because there is no thermal etching between the pulses. This allows the measurement of the ion-enhanced erosion rate of a fully chlorinated GaAs-surfaces at technical relevant conditions.

CONCLUSIONS

The CAIBE process is suitable for achieving high etch rates. However, the basic mechanism behind this process are very complex and the interaction between the physical and the chemical etching is not fully understood. In this study it is assumed, that the momentum transfer from the kinetic inert gas ions to the sample surface causes an ion-enhanced erosion. This resulting thermal energy is sufficient enough to outperform the required activation energy for chemical reactions and/or desorption of the reaction products. The temperature dependence of the chlorine CAIBE process of GaAs has been studied. In general, the surface temperature has a strong influence on the etch behaviour. It could be established that at temperatures up to 300 K only the ion induced enhancement will cause an increased etch rate, whereas at temperatures above 300 K a thermal etching occurs additionally. In conclusion, a precise control of the surface temperature is very important for the CAIBE process. Thus water cooling with helium back side coupling proved to be suitable for the prevention of unintended sample heating during ion beam exposure. Consequently, an additionally thermal influences on the etch rate could be excluded and the results were more reproducible. The usage of a beam chopper allowing the control of the pulse conditions in terms of the frequency and the PLM of the ion beam. This offers new additional possibilities of influencing the CAIBE process to the requirements of industrial requests. First results show, that with decreasing pulse length modulation the total ion beam exposure time could be reduced for the same etch depth. Both, the damage of the surface as well as the side wall angle, might be improved at a consequence. In addition, a reduced thermal effect of the ion beam can be expected.

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FIGURES

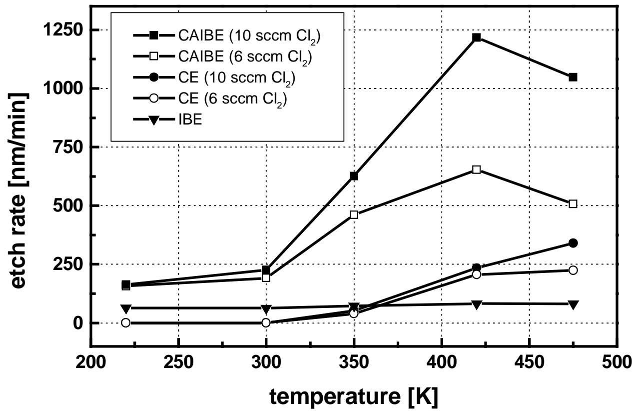

Figure 1: Etch rate depending on the surface temperature of GaAs for different etch conditions. For IBE and CAIBE the ion beam density was normalised to 0.5 mA/cm^2 at an ion beam energy of 400 eV.

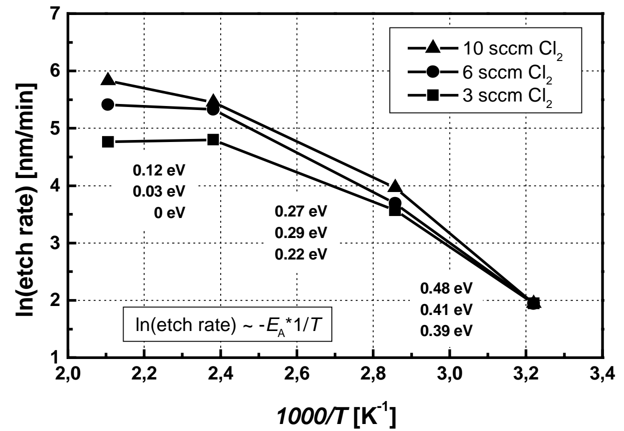

Figure 2: Arrhenius plot for the chemical etching (CE) of GaAs with chlorine. The values below the curves correspond to activation energy E_A of the desorption process.

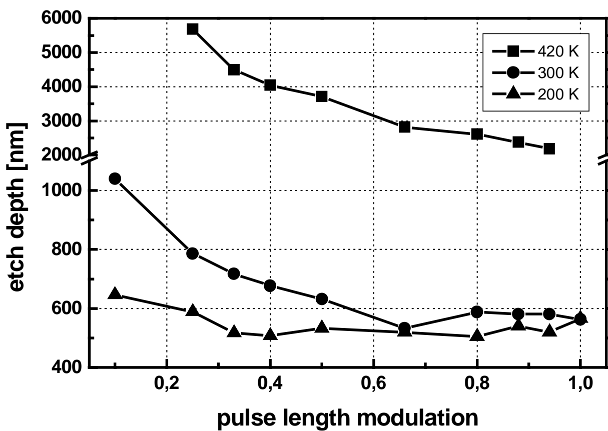

Figure 3: Etch depth depending on the PLM at different surface temperatures. The ion beam exposure time per pulse was fixed at 0.1 ms for all experiments. The total ion beam exposure time was 200 s at an ion beam energy of 400 eV, an ion current density of 0.5 mA/cm^2, and a chlorine flux of 6 sccm.