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THERMAL AND ION-ASSISTED REACTIONS OF $Al_{0.3}Ga_{0.7}As$ WITH MOLECULAR CHLORINE

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ABSTRACT

Reaction of $Al_{0.3}Ga_{0.7}As$ with molecular chlorine was studied with and without simultaneous bombardment by energetic argon ions. The reaction products signals were measured as functions of surface temperature. For the purely thermal reactions, the main products below 600 K were $AlCl_3$, $AsCl_3$ and $GaCl_3$. The etching rates were two orders of magnitude lower than those of pure GaAs. With simultaneous ion bombardment, the reaction product signal of $AsCl_3$ at room temperature increased by almost a factor of four over the corresponding thermal reaction signal. The comparable enhancement factor for pure GaAs was ~6.

INTRODUCTION

Because of the close lattice match between AlGaAs and GaAs, hetrojunctions fabricated of these materials are used extensively for many applications, such as modulation-doped field effective transistors, injection lasers and solar cells. Selective dry etching techniques are of great utility in achieving small-device geometry of such devices.

In spite of technological advances in dry etching [1-3] substantial efforts are still required for understanding the etching process at a fundamental level. This is due to the fact that practical etching involves a complex combination of chemical reactions and physical sputtering or damage production in the presence of a mixture of chlorinated gases to achieve material removal.

In continuing of the study of gallium arsenide/Cl_2 reactions [4], the present work addresses the etching of $Al_{0.3}Ga_{0.7}As$ with the molecular chlorine. The thermal and ion-induced reactions investigated by modulated molecular beam techniques reported here are intended to elucidate some of the basic details of the etching process in a simple, well-characterized system.

EXPERIMENTAL

The reaction is studied by modulated molecular beam mass spectrometry. Modulation of the incident Cl_2 reactant coupled with phase-sensitive detection of the output signals improves the signal-to-noise ratio, assists in identification of the reaction products and, most importantly, provides information on the time delays due to surface reactions.

The basic features of the apparatus have been described in detail elsewhere [4]. Briefly, the system (Fig. 1) consists of three differentially-pumped vacuum chambers separated by orifices, whose function is to form collimated molecular beams from the diffuse fluxes of molecules in the upstream chambers. In the first chamber, the Cl_2 flux is generated by effusion from a hole in the end of a quartz tube containing chlorine gas at a few Torr pressure. The flux is modulated by a rotating toothed disk. The small portion of this flux which passes through the orifice leading to the second

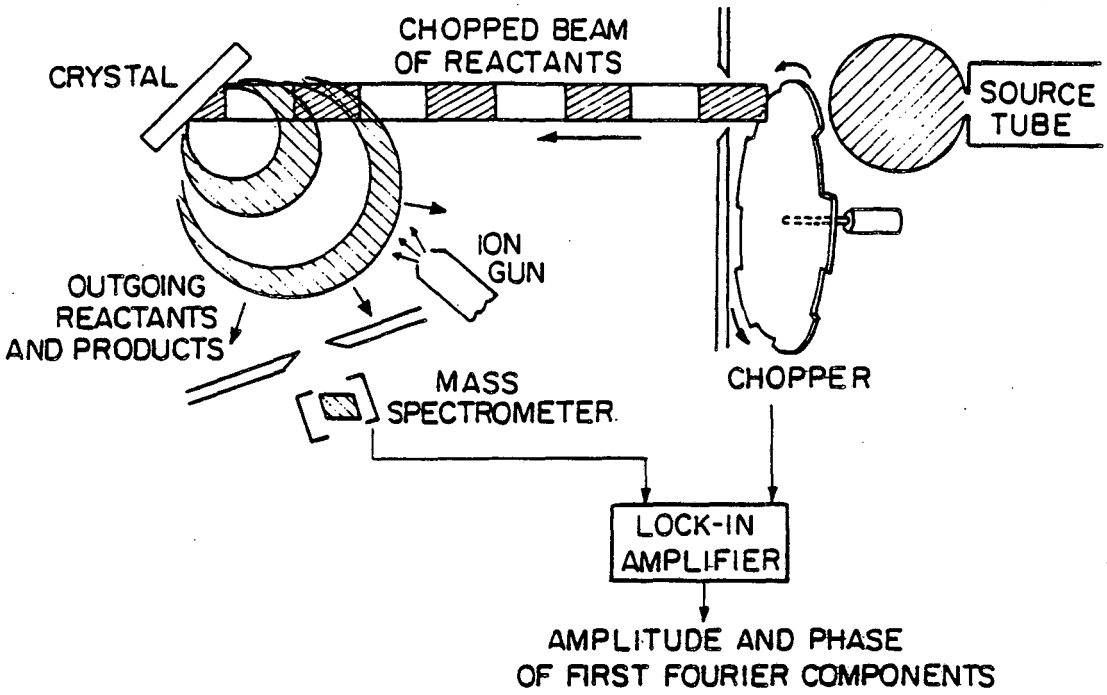

Figure 1. Schematic Representation of the Modulated-Beam Reactive Scattering Apparatus

chamber constitutes the modulated molecular beam of reactant molecules. It is about 1.5 mm in diameter and impinges directly on the surface of the $Al_{0.3}Ga_{0.7}As$ crystal mounted in this chamber. The crystal is heated by radiation from a hot filament and its surface can be bombarded by an ion beam either for cleaning or for studying ion-assisted reactions.

Part of the reactant beam merely scatters from the surface without interaction. The rest chemisorbs on the surface and eventually reappears as a volatile chloride of aluminum, gallium or arsenic. Small fractions of the reflected (scattered) reactant beam and the desorbed reaction products which have been produced by reactions on the surface pass in free-molecule flow through an orifice leading to the third chamber, which houses a quadrupole mass spectrometer with a line-of-sight view of the reaction spot on the crystal surface.

The output from the mass spectrometer is processed by a lock-in amplifier to yield the first Fourier components of the modulated, mass-analyzed signals from the scattered reactant or from the reaction products emitted from the crystal surface.

The sample is provided by Hewlett Packard. It consists of a AlGaAs layer, $\sim 1\mu m$ thick, grown by molecular beam epitaxy (MBE) on (100) oriented semi-insulating GaAs substrate.

The results reported here are for a fixed modulation frequency of 20Hz and an incident chlorine molecular beam intensity of 5×10^{16} molecules/cm^2s (equivalent to a chlorine pressure of 4×10^{-4} Torr at the target). The modulated feature of the method has been used principally to improve the signal-to-noise ratio of the output signals.

RESULTS

Thermal Reaction

In the absence of cracking patterns in the literature for arsenic,

gallium and aluminum chlorides, the temperature dependence and phase lags of all detectable signals are used to infer the nature of the actual reaction products [4]. Up to 600K, the main products are the trichlorides. These, however, crack mostly to dichloride ions in the mass spectrometer with 70ev electrons energy. Above 600K, gallium and arsenic monochlorides are also detectable, but no AlCl was found.

Figure 2 shows the temperature dependences of $GaCl_2^+$ and $AsCl_2^+$ normalized with respect to the Cl_2^+ signals on $Al_{0.3}Ga_{0.7}As$. The corresponding

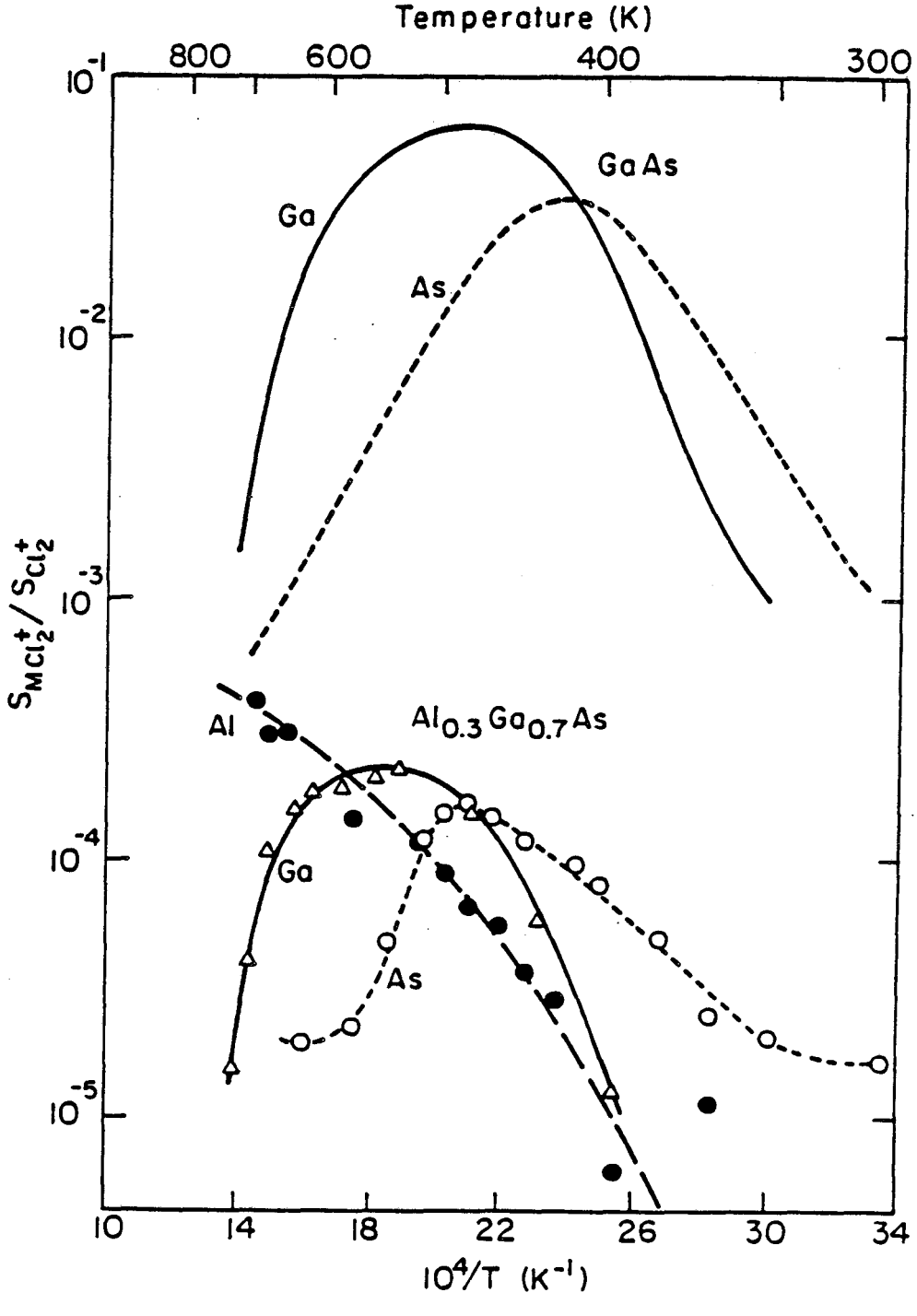

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Figure 2. Arsenic and gallium and aluminum dichloride ions detected mass spectrometrically as a function of surface temperature. The points are the results on $Al_{0.3}Ga_{0.7}As$ and lines on GaAs.

signals for pure GaAs are also shown in the figure for comparison. The general temperature dependence of the signals on both GaAs and $Al_{0.3}Ga_{0.7}As$ are similar, but the amplitudes for aluminum containing gallium arsenide are about two orders of magnitude lower than pure gallium arsenide and their maximums are shifted toward higher temperatures. The temperature dependence of $AlCl_2^+$ signal is also shown in Fig. 2. The reactivity of this ion increases monotonically with temperature up to 700K studied, but is otherwise of the same magnitude as the gallium and arsenic signals.

Ion-Induced Reaction

Figure 3 shows the response of the reflected chlorine and $AsCl_2^+$ signals during reaction at 300K due to a constant incident Cl_2 beam and simultaneous bombardment of the reaction spot on the crystal of 3.5 KeV argon ions at a current density of $20\mu A/cm^2$. The two plots represent different experiments. The upper plot shows that when the ion beam is turned on, the reflected chlorine signal drops by about 1%. Conversely, the lower plot shows that when ion bombardment is stopped, the $AsCl_2^+$ signal shows a rapid decrease of about 30% followed by an exponential decrease which approaches a new steady state. The ratio of the signal with and without ion-assistance is approximately four. Similarly, when the ion is turned on, a rapid increase in signal is observed, followed by increase toward the original ion-assisted steady state reaction. Similar behavior (except for the magnitude of the decrease in the Cl_2^+ signal) was found for the GaAs reaction. The long-term decrease of the $AsCl_2^+$ signal is probably due to accumulation of impurities on the surface from the vacuum system.

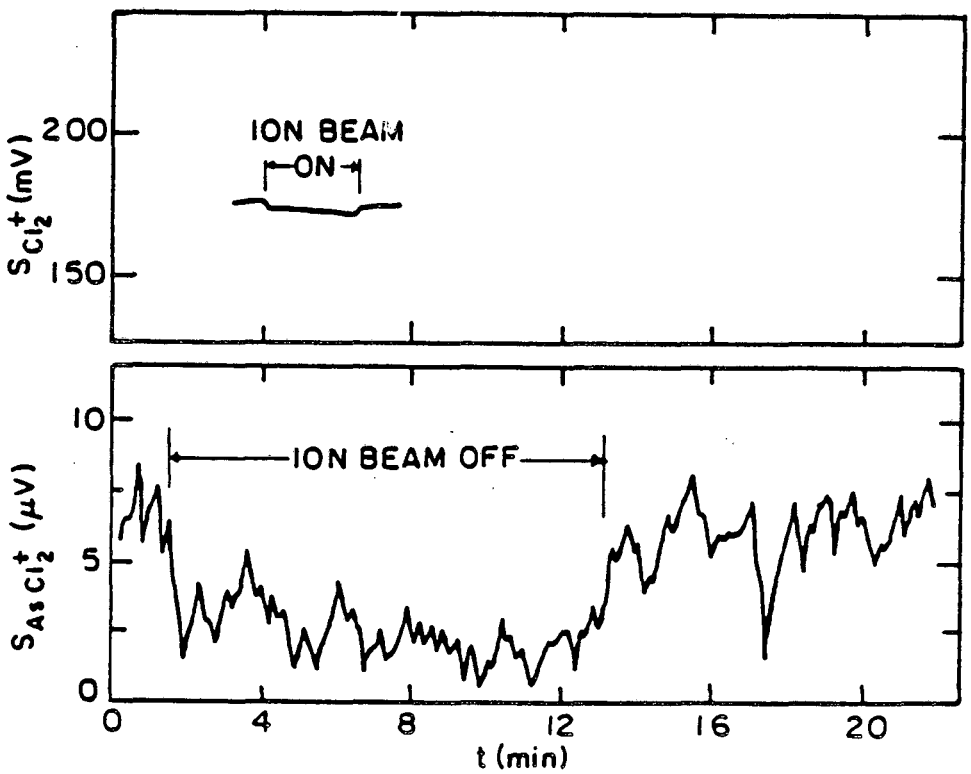

Figure 3. Effect of ion bombardment on the reflected chlorine and arsenic chloride signals at room temperature.

DISCUSSION

In developing sophisticated hetrojunction devices, selective dry etching can provide the desired capabilities of anisotropy and a wide range of depth profiling. It is essential, however, that the process of etching introduce minimal damage.

Comparing the thermal and ion-enhanced processes, it can be concluded, from this and earlier [4] work, that both can provide excellent etching rates and selectivity (the ratio of etching rates of GaAs to $Al_{0.3}Ga_{0.7}As$). The main advantage of ion-enhanced process is that it can provide desirable anisotropy. However, considerable damage has been observed in GaAs after ion-assisted etching [5,6] due to energetic ions. For shallow etching (e.g., a process used in HEMT) thermal etching may therefore be preferred over the ion-assisted etching. The present data show that the increase reaction rate at temperature ~150K above room temperature is larger than achievable by ion bombardment.

It is surprising to observe that the only effect of aluminum addition to GaAs is to greatly reduce the etching rate. Reduction of sticking probability of Cl_2 on the surface is a possible explanation. Another Explanation is that the $AlCl_3$ species is much less volatile than the other two trichlorides and hence its volatilization controls the desorption rates of the other two gaseous products.

It should be noted that the relative magnitudes of the $AsCl_2^+$ signals with and without ion assistance does not necessarily reflect the etching rate ratio. This is due to the fact that the signal of mass spectrometer is proportional to the density at the ionizer. Recent results of McNevin and Becker [7] suggest that the ion assisted products desorb with velocity distribution close to Maxwellian with temperature of about 1600K. Utilizing this figure, the ion-assisted amplification factor may be as high as $\sqrt{1600/300}$ = 2.3 times greater than that inferred from Fig. 3.

CONCLUSION

1. Both thermal and ion-assisted etching can provide excellent selectivity between GaAs and $Al_{0.3}Ga_{0.7}As$.
2. For thermal reactions, the main detectable products up to 600K are $AsCl_3$, $GaCl_3$ and $AlCl_3$.
3. The main effect of aluminum is to depress the reaction rates, both thermal and ion-assisted, by about two orders of magnitudes.

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