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The Thermal and Ion-Assisted Reactions of GaAs(100)

with Molecular Chlorine

by

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ABSTRACT

Reaction of single-crystal GaAs with molecular chlorine was studied with and without simultaneous bombardment by energetic argon ions. The reaction was detected by an in-situ mass spectrometer; reflected chlorine and reaction product signals were measured as functions of crystal temperature.

For the purely thermal reaction, the main products below surface temperatures of 550 K were $AsCl_3$ and $GaCl_3$. At higher temperatures, the monochlorides were the dominant volatile products. A maximum reaction probability of 0.3 was observed at 450 K for trichloride production.

With simultaneous ion bombardment, the reaction rate at room temperature increased by almost a factor of six over the thermal reaction rate. A factor of three increase was observed at the same time that the ion beam was turned on. This was followed by a gradual increase by another factor of two over a period of several minutes. This effect of ion enhancement was attributed to initial removal of a gallium-rich chloride scale formed on the surface during the thermal reaction followed by gradual accumulation of radiation damage to the surface. Both of these processes are expected to increase the rate of substrate volatilization.

I. Introduction

Etching of semiconductor materials using dry methods is of great interest for high-resolution, high-fidelity patterning. Recently, reactive-ion etching[1], reactive-ion-beam etching[2] and ion-beam-assisted etching[3], all using chlorinated vapor reactants, have been applied to fabrication of GaAs devices. In spite of these technological advances, understanding of the etching process on a fundamental level is rudimentary. This is mainly due to the fact that practical etching involves a combination of chemical phenomena and physical sputtering or damage production in the presence of a mixture of chlorine-containing gases to achieve material removal. The complexity of these processes precludes the use of such experiments for the understanding of the mechanisms responsible for etching.

The thermal and ion-induced investigation of the etching of GaAs by molecular chlorine reported here is intended to elucidate some of the basic details of the etching process in a simple, well-characterized system.

II. 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 else-where[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 chamber constitutes the modulated molecular beam of reactant molecules. It is about 3 mm in diameter and impinges directly on the surface of the GaAs crystal mounted in this chamber. Because of the high vacuum environment, homogeneous gas phase reactions are absent and there are no wall effects to consider. 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 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. Because scattered chlorine spends no time on the surface, it appears in the output in the square-wave shape imparted to it by the mechanical chopping. The reaction products, however, usually are emitted with a time delay due to the finite speed of the surface reaction. This nonzero residence time results in a waveform which is distorted from the original square-wave. When Fourier-analyzed by the lock-in detector, this shape difference produces a phase lag with respect to the first Fourier component of the reflected chlorine signal. This phase lag contains information directly related to the kinetics of the chemical reactions on the crystal surface, provided that the time scale of the reactions are comparable

to that of the period of the modulation of the incident beam (20 Hz). If
the reactions are fast compared to the period of beam modulation, all kinetic
information is lost, and the experiment is equivalent to a steady (DC)
molecular beam system. If the reaction is very slow compared to the beam
modulation period, all information is lost because the modulated(AC)
component of the signal, to which the detection system responds, vanishes.
In the present case, the arsenic chloride products approach the former limit
while the gallium chloride products are highly demodulated, so much so that
they are barely detectable when the crystal is at 300 K.

The results reported here are for a fixed modulation frequency of 20 Hz
and an incident chlorine molecular beam intensity of 5×10^{16} molecules/cm^2-s
(equivalent to a chlorine pressure of 2×10^{-4} Torr). Crystal temperatures
between 300 and 700 K were investigated. Only the observations of the
signals from the chlorides of arsenic are reported. This product showed
little change in phase lag over the temperature range tested, so that the
signal amplitudes were not affected by demodulation due to very slow surface
reactions. Essentially, the modulated feature of the method has been used
principally to improve the signal-to-noise ratio of the output signals.
The gallium chlorides were detected, but with large phase lags, which
indicate slow rates of formation on the surface compared to the volatile
arsenic compounds. A complete mechanistic study of the reaction requires
analysis of the phases and amplitudes of both volatile products, and will
be reported in a future publication.

III. Results

A. Reflected Chlorine Signal

An important measure of the extent of the reaction is obtained by
monitoring the decrease in the scattered Cl_2 signal as the crystal tempera-
ture is raised while the intensity of the incident beam remains constant.

The reflected Cl_2 signal always decreases with increasing surface temperature, but for two possible reasons. The first, and the one from which information relevant to the surface chemistry can be extracted, is because the portion of the incident beam which chemisorbs on the surface reacts to form one of the volatile chlorides of the substrate elements. When this occurs, the reflected Cl_2 signal decreases and is accompanied by an increase in the signals due to the volatile products which contain chlorine.

The second reason for a decrease in the magnitude of the reflected Cl_2 signal with increasing temperature arises from interactions with the surface which result in energy transfer from the substrate to the room-temperature incident molecules. The reflected molecules possess a translational temperature somewhere between the original 300 K and the temperature of the surface. This energy transfer process is described by the thermal accommodation coefficient:

$$\alpha_{th} = \frac{T_{refl} - 300}{T - 300} \tag{1}$$

where T_{refl} is the temperature of the reflected Cl_2 molecules and T is that of the surface.

Because the mass spectrometer responds to the density (rather than to the flux) of molecules in the ionizer, the hotter, faster moving molecules produce a signal which differs from that for room temperature molecules by the formula:

$$\frac{S(T)}{S(300)} = (\frac{300}{T_{refl}})^{1/2} = [1 + \alpha_{th}(\frac{T}{300} - 1)]^{-1/2} \tag{2}$$

where S(T) is the measured signal when the surface is at temperature T. If the thermal accommodation coefficient is unity, the signal of the reflected chlorine from a surface at 700 K would be 35% smaller than that for a surface at 300 K.

The observed effect of surface temperature on the magnitude of the scattered Cl_2 signal is shown in Fig. 2 in terms of the quantity:

$$\epsilon_T = 1 - S(T)/S(300) \qquad (3)$$

For the following reasons, the data shown in Fig. 2 are believed to be due to chlorine removal due to surface reactions rather than to the thermal accommodation effect discussed above. First, the data show structure not expected from simple thermal accommodation, which would result in a monatonically increasing curve with increasing surface temperature. If the value of ϵ_T at the trough at 550 K were due entirely to thermal accommodation effects, Eqs(2) and (3) show that $\alpha_{th} \backsimeq 0.13$ However, as will be shown later, appreciable reaction product is observed at this temperature, so the thermal accommodation coefficient must be even smaller than the value estimated above. The data in Fig. 2 are believed to reflect changes in chemical reactivity due to surface temperature. The quantity ϵ_T thus represents the total reaction probability, which is the fraction of the incident Cl_2 molecules which chemisorb on the surface and return to the gas phase as a volatile chloride of arsenic or gallium.

In addition to thermal accommodation effects, changes in the angular distribution of the scattered Cl_2 is a possible source of the observed decrease in the reflected signal with increasing surface temperature. Because the apparatus has no provision for measurement of the angular distribution of molecules emanating from the beam spot on the surface, this possibility could not be directly assessed. However, the arguments presented above indicate that thermal accommodation of incident chlorine with the surface is poor for all surface temperatures. This observation suggests that the angular distribution of the scattered chlorine molecules, which, like thermal accommodation, is related of gas-solid energy transfer, is

probably not significantly altered as the surface temperature changes.

B. Volatile Reaction Products

Because of fragmentation by the 70eV electrons used to ionize the neutral species entering the mass spectrometer, identification of the reaction products requires care. No cracking patterns for volatile arsenic and gallium chlorides are available in the literature. Nor is it feasible to independently measure the cracking patterns in the same system used for the reaction studies because this would require use of significant quantities of potential reaction products such as $AsCl_3$ and $GaCl_3$ in the apparatus. Despite the signal-to-noise improvement afforded by beam modulation, the residues of these chemicals would significantly degrade the quality of the data obtained during the reaction experiments. However, the temperature dependence and phase lags of the signals can be used to infer the nature of the actual reaction products.

The ions $AsCl_3^+$ and $AsCl_2^+$ and $AsCl^+$ were observed in the mass spectrometer. As shown in Fig. 3, all three exhibited identical temperature dependences up to 500 K. This behavior strongly suggests that all arose from the same parent, namely, $AsCl_3$. However, at higher temperatures, the dominant signal was $AsCl^+$, which appears only as the parent ion.

Similar behavior was observed for the gallium-containing ions observed in the mass spectrometer. However, these signals showed considerably larger phase lags than their arsenic counterparts, indicating that the kinetics of the surface reaction was controlled by production of the volatile gallium chlorides rather than by the rates of formation of $AsCl_3$ or $AsCl$.

The data presented in Figs. 2 and 3 are self-consistent. The maximum in the total reaction probability at 450 K inferred from the scattered chlorine signals in Fig. 2 is due to the peak in the trichloride production rate shown in Fig. 3 at the same temperature. The valley at 550 K in Fig. 2

corresponds closely to the minimum in the signals of the arsenic chlorides in Fig. 3.

It is difficult to detect atomic or molecular chlorine desorbed directly from the surface because ionization of the scattered chlorine molecules in the mass spectrometer produces both Cl^+ and Cl_2^+. However, no evidence of significant desorption of chlorine from the surface was obtained.

C. Ion-Assisted Reaction

Figure 4 shows the response of the reflected chlorine and $AsCl_3$ signals during reaction at 300 K due to a constant incident Cl_2 beam and simultaneous bombardment of the reaction spot on the crystal by 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 was turned on, the reflected chlorine signal dropped immediately by about 8%, indicating increased production of volatile As and Ga chlorides. Conversely, the lower plot shows that when ion bombardment is stopped, the $AsCl_3$ signal shows an instantaneous decrease of about 30% followed by an exponential decrease which approaches a new steady state. The ratio of the etching rates with and without ion-assistance is approximately six. Similarly, when the ion beam is turned on, an instantaneous factor of three increase in reaction rate is observed, followed by increase towards the original ion-assisted steady state rate.

During the period that the $AsCl_3$ signals were recorded, no $GaCl_3$ signal was observed, with or without ion bombardment. This negative result does not imply that $GaCl_3$ was not forming and evaporating; it simply means that the evaporation rate was unresponsive to the modulated driving force of the incident Cl_2 beam. The $GaCl_3$ emission rate is predominantly steady state, and is not detected by the lock-in amplifier. The detection system sees only the modulated portions of the signals, and thus responds preferentially

to $AsCl_3$, which, because of its relatively high vapor pressure, is much more responsive to the periodic changes in the incident Cl_2 beam intensity.

IV. Discussion

Although the mechanistic details of the thermal etching of GaAs by chlorine gas have not been worked out, the present data offer some insight concerning the role of the bombarding energetic ions.

It has been inferred from the large phase lag of the gallium chloride signals during thermal etching that the formation and desorption of this species is the rate-limiting process in the overall reaction. This conclu- sion is consistent with the lower vapor pressure of $GaCl_3$ compared to that of $AsCl_3$. Since the etching process must remove As and Ga atoms in equal numbers, it follows that the surface during Cl_2 exposure is enriched in gallium to the extent necessary to produce equal vaporization rates of the two trichlorides. Or, a scale of gallium-rich chlorides exists on the surface during the thermal reaction.

The initial effect of turning on the ion beam during reaction is to clean this scale from the surface. Since it can be shown that the tempera- ture rise of the surface due to ion bombardment is less than a degree, the cleansing action of the beam is not a simple thermally-activated process of desorption of a relatively nonvolatile species. Whatever the mechanism of scale removal, the cleansed surface exposes arsenic-rich solid to the inci- dent chlorine, which permits the reaction to proceed at a factor of about three times faster than on the surface which supported the gallium-rich scale.

The subsequent slow rise of the $AsCl_3$ desorption rate following initia- tion of ion bombardment can be due to one of at least two causes: either it represents the slow removal of more strongly bound impurities (oxygen, carbon) from the surface, or it is a result of accumulation of surface damage

from the impinging ions. While it is not possible without simultaneous surface analysis to discard the former cause, a simple damage annealing-production model can explain the long transients seen in Fig. 4 following initiation or termination of ion bombardment.

·Let N^* be the concentration of active sites on the surface on which the $As-Cl_2$ reaction proceeds more rapidly than on normal sites. It is also assumed that the probability of this reaction is proportional to the concentration of sites, so that the shape of the transients in Fig. 4 reflect the temporal behavior of N^*. The time rate of change of the active site density is given by:

$$\frac{dN^*}{dt} = \sigma I - k_a N^*$$

where I is the current density of the ion beam, σ is the probability that an incident ion creates an active site and k_a is the rate constant for thermal annealing of these sites. When the ion beam has been on for a long time, a steady-state active site concentration is obtained:

$$N_{ss}^* = \sigma I/k_a$$

when the beam is turned off, the site concentration decays according to:

$$N_{off}^* = N_{ss}^* \exp(-k_a t)$$

Assuming that the active site concentration after long periods of thermal reaction is small compared to N_{ss}^*, the accumulation of damage after the beam is turned on is given by

$$N_{on}^* = N_{ss}^* [1 - \exp(-k_a t)]$$

If the instantaneous signal changes (due to rapid accumulation or removal of a gallium-rich chloride scale) are neglected, the transients shown in the trace on the bottom of Fig. 4 are well represented by the above equations with $k_a^{-1} \simeq 4$ min.

An observation which supports the notion that the slow transients in reactivity seen in the bottom graph of Fig. 4 are related to creation and removal of active sites due to ion bombardment is the constancy of the phase lag of the AsCl signal. This behavior usually means that the initial step in the reaction (such as the sticking probability of Cl_2 to the crystal surface) is changed but the kinetics of the subsequent surface processes, which impart the phase lag to the emitted product, are unaffected by the ion impingement.

From the point of view of device fabrication, ion-assisted etching offers two advantages over thermal reaction etching. First, ion bombardment generally accelerates the chemical etching process, which is desirable for production efficiency. In the present system, ions enhance the rate by a factor of about 6 at room temperature. If this were the only feature to be considered, Fig. 3 shows that greater enhancement of the room-temperature reactivity can be achieved simply by heating the crystal to 450 K.

The second desirable feature of ion-enhanced chemical etching is that it can provide desirable anisotropy to the etching process. In digging slots, for example, an ion beam incident normal to the surface will enhance the reactivity of the bottom surface of the slot without affecting the vertical walls, thus permitting high aspect ratio trenches to be fabricated. However, the atomic damage to the crystal produced by ion bombardment degrades device performance. Considerable damage has been observed in GaAs after sputter-etching(5) and following ion-assisted etching(6,7). This ion-induced damage cannot be completely removed by thermal annealing up to 800 K. Instead, the damaged region (usually less than a micron deep) can be removed by a subsequent wet-etching step. However, dry etching to remove the surface damage is an alternative. This can be accomplished simply by heating the specimen to 450 K (where the thermal reaction probability is 0.3), which will remove 1 micron of the surface in less than 10 minutes.

V. Summary

1. Thermal accommodation of chlorine molecules scattered without reaction form the surface of single crystal GaAs (including any scale that may be present due to the reaction) is quite small, probably less than $\sim$0.13.

2. The total reaction probability for the thermal reaction of Cl_2 and GaAs is less than 0.01 at room temperature but increases to 0.3 at 450 K. This maximum is associated with the emission of $AsCl_3$ and $GaCl_3$. The trichloride reaction rate decreases sharply at higher temperatures but etching continues at high rates due to production of the monochlorides. The total reaction probability attains a value of $\sim$0.5 at 700 K and shows little sign of levelling off at higher temperatures.

3. The mono- and trichlorides are the only reaction products. They are produced in distinct temperature ranges.

4. At 300 K, ion bombardment accelerates the etching rate by a factor of about six. The mechanism appears to include, in roughly equal measure, rapid removal of a scale of relatively nonvolatile gallium sub-chlorides from the reacting surface followed by slow enhancement of the reactivity of the exposed substrate either due to damage accumulation or by impurity removal. The characteristic time constant of the latter step is on the order of minutes.

5. The high thermal reaction probability at 450 K suggests a simple method for removing atomic damage in areas previously etched with the aid of ion bombardment.

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Figure Captions

1. Experimental apparatus.

2. Variation of the reflected chlorine signal as a function of surface temperature.

3. Arsenic chloride ions detected mass spectrometrically as a function of surface temperature.

4. Effect of ion bombardment on the reflected chlorine and arsenic chloride signals at room temperature. Constant modulated molecular beam of chlorine on the crystal surface.
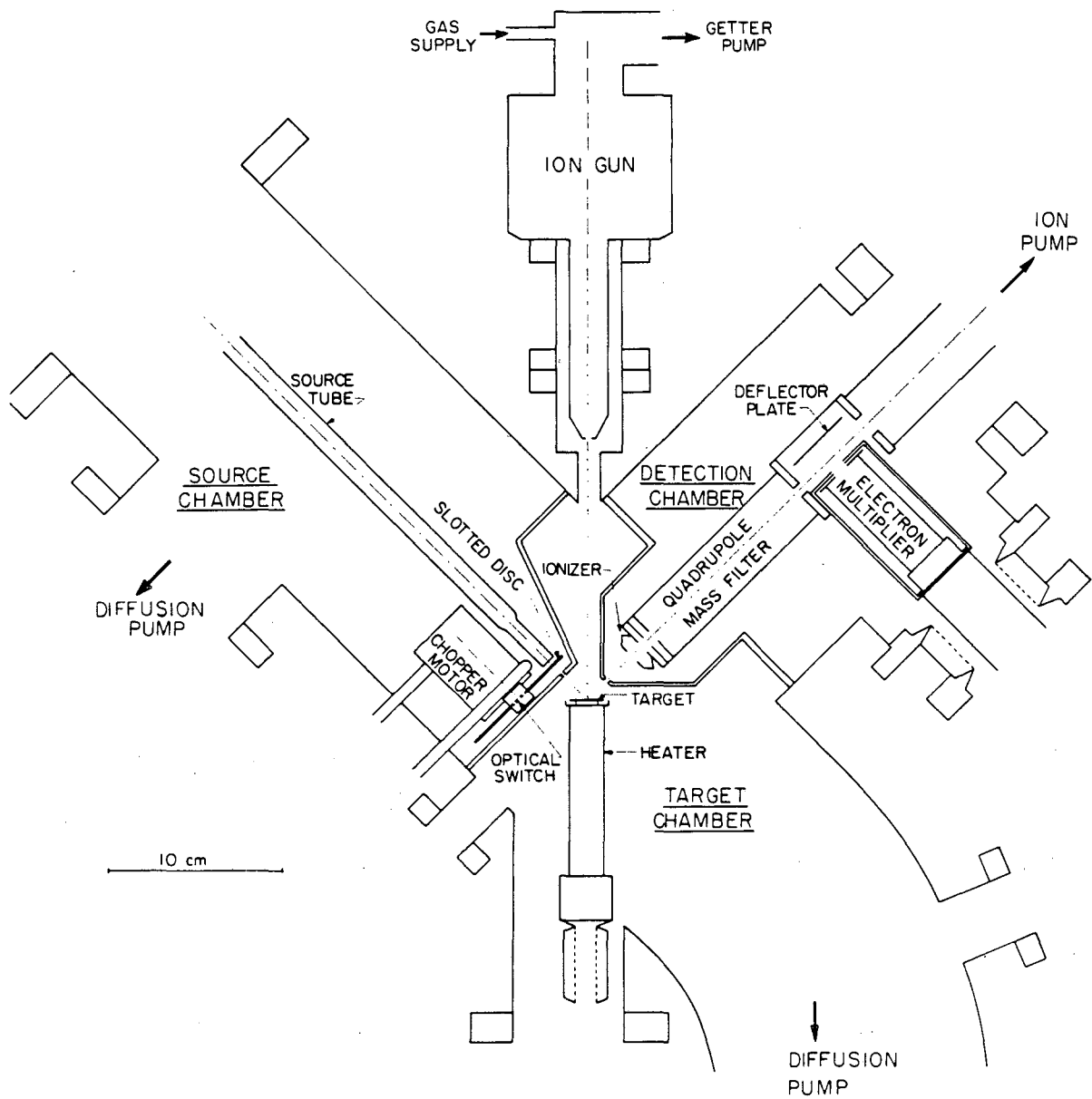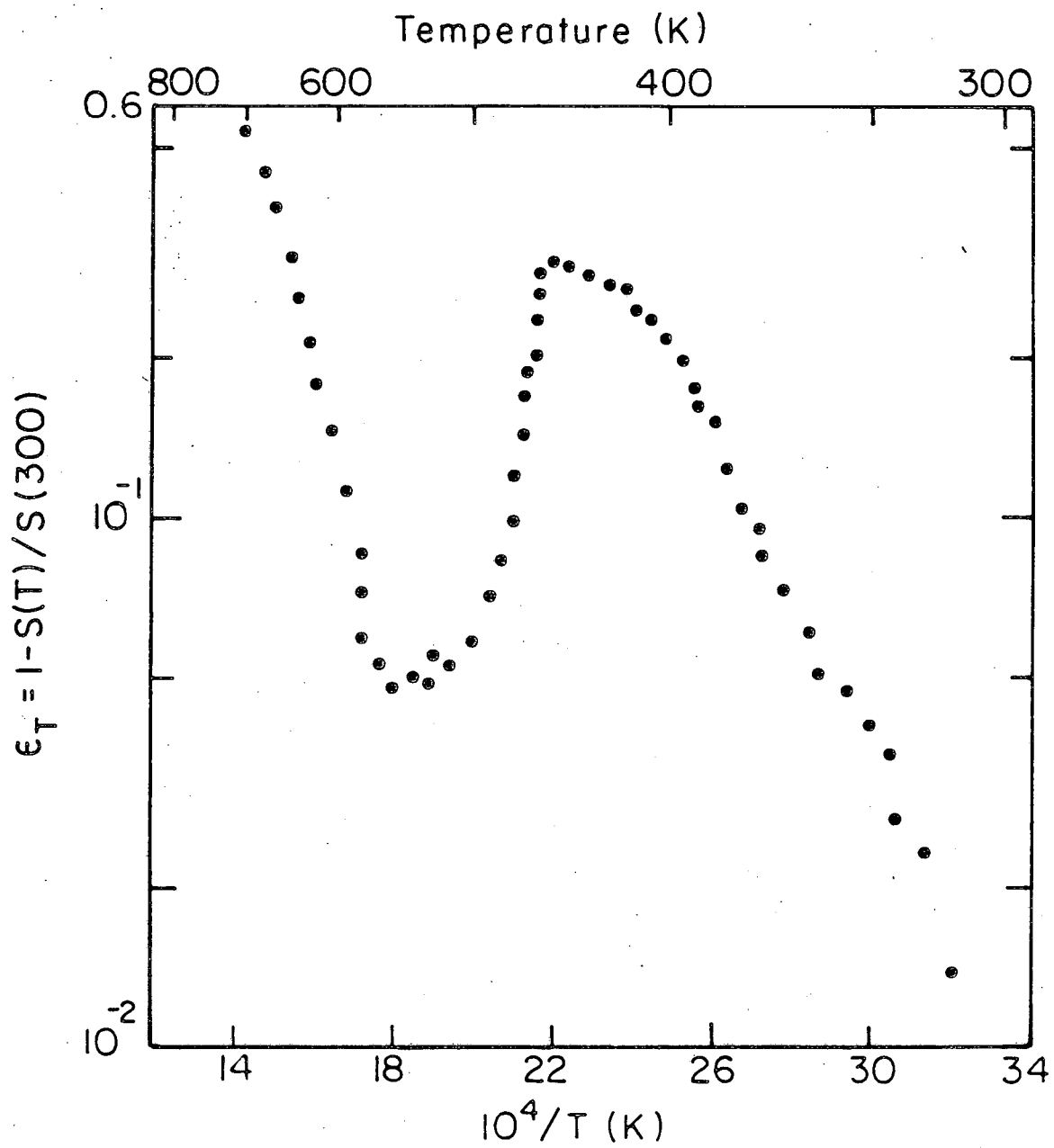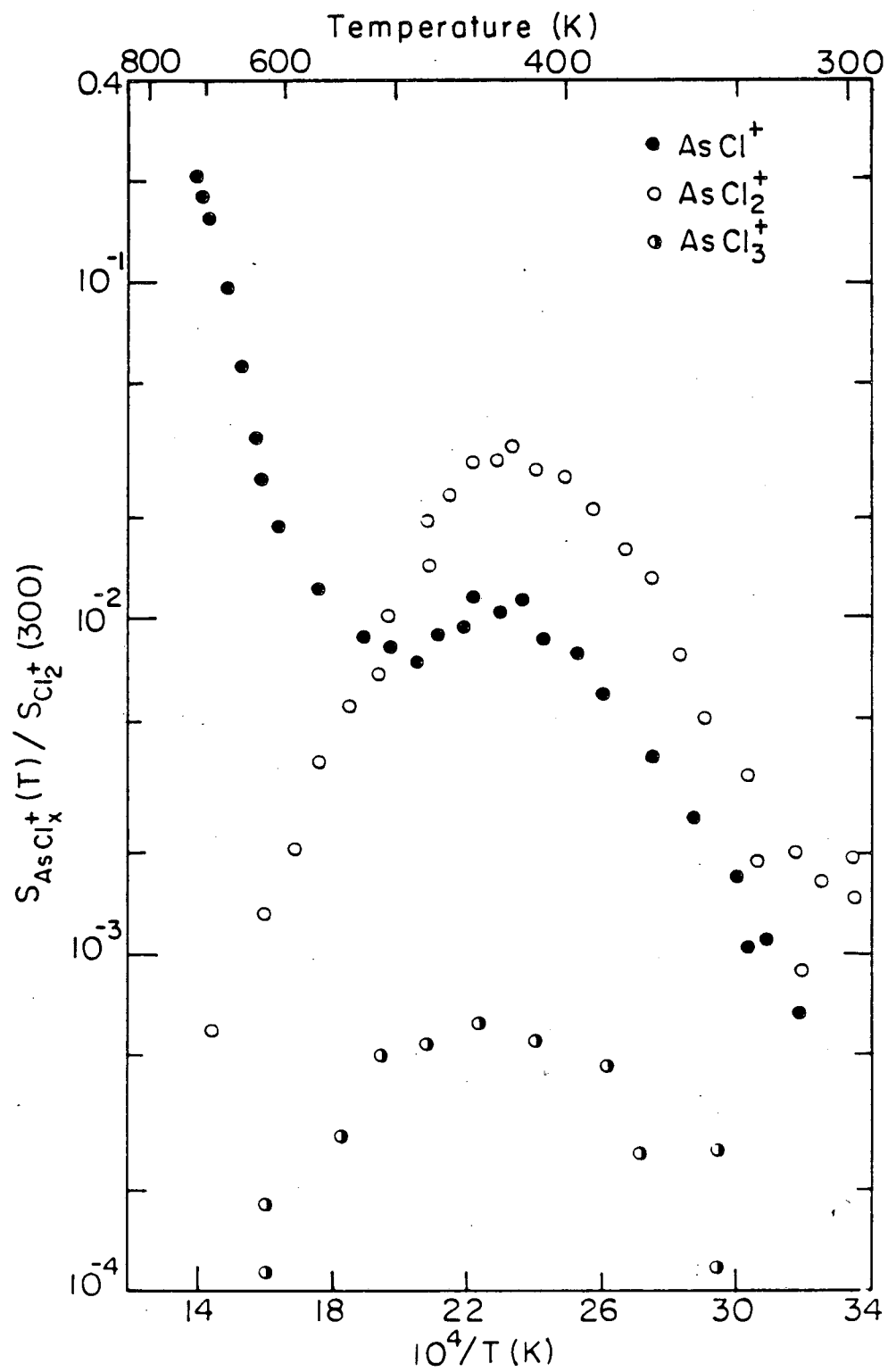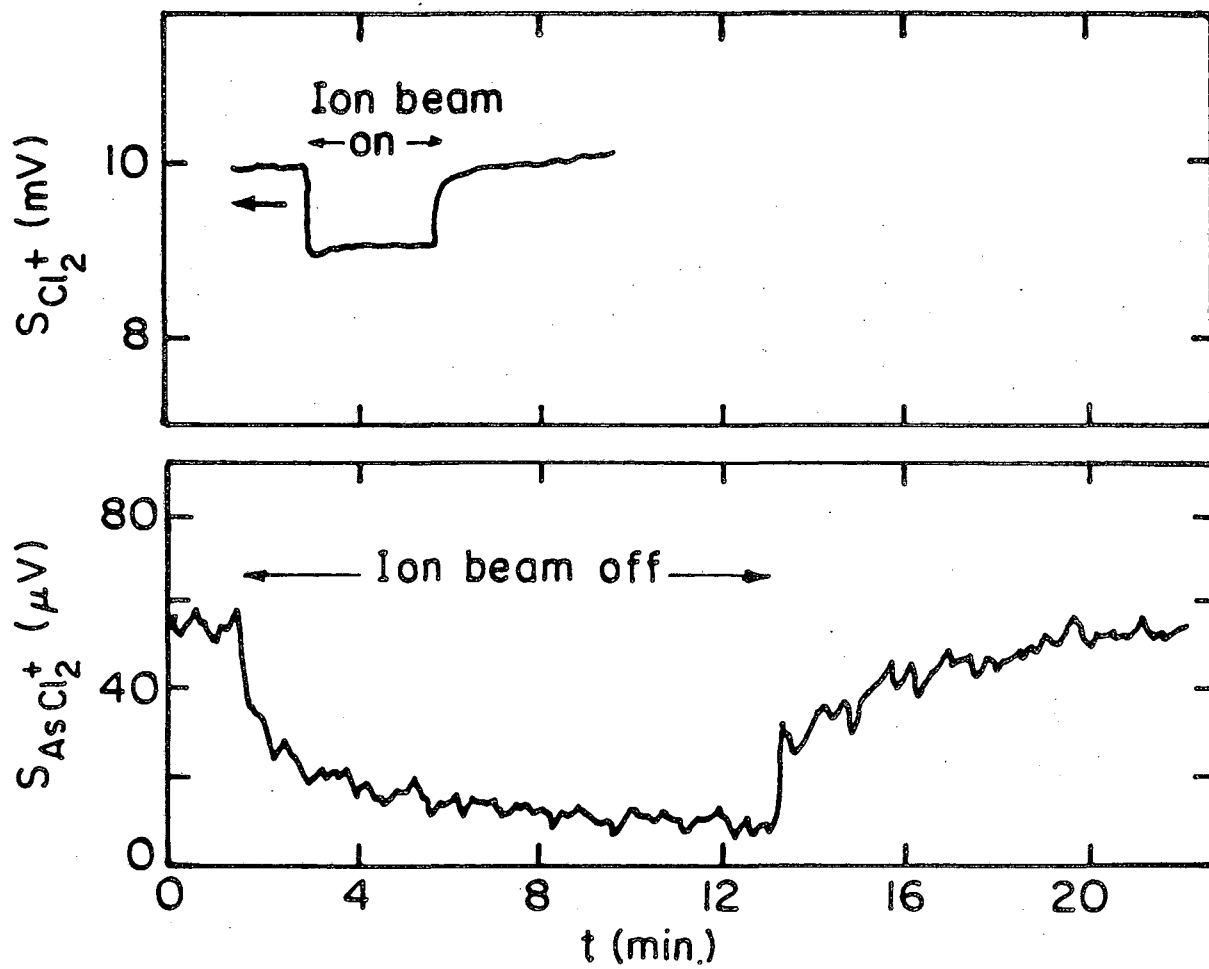
Figure 1.

XBL 751- 5501A

Figure 2.

XBL 857-6410

Figure 3.

XBL 857-6411

XBL 857-6412

Figure 4.