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Energy dependence of the reaction rate constants of Ar^+ , Ar^{++} and N_2^+ ions with Cl_2

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Introduction

Dry etching processes using low temperature plasmas in Cl_2 and in Cl_2 -noble gas or nitrogen mixtures are common in the manufacture of semiconductor devices, but their chemical mechanisms are often poorly understood. It was shown by F.X. Campos et al [1] that hyperthermal Cl_2 etches room temperature silicon at least ten times faster than thermal Cl_2 and that the etching rate increases significantly at Cl_2 kinetic energies larger than 3 eV. More detailed analysis of neutral mean kinetic energy of Ar, N_2 , Cl_2 in ECR plasma source has been carried out by R.S. Goodman et. al. [2]. This energy was varied between 0.04 and 0.45 eV. Enhancement in neutral mean kinetic energy has shown a strong correlation with ion fluxes of atomic and molecular species out of the source for all source gases studied. The average translation energy of Cl^+ ions (determined by LIF Doppler method) gave values in the range 0.24 – 0.61 eV. [3] These values depend also on the gas pressure. It is surprising, but till now only S.G. Lias [4] has measured some reactions of positive inert gas ions with chlorine by ICR method. No other reaction rate coefficient can be found in review papers [5,6] besides our previous reported value [7]. Therefore the aim of this paper is to present the results of the reaction rate constant measurements of Ar^+ , Ar^{++} , N_2^+ ions with chlorine as a function of mean relative kinetic energy.

Experimental apparatus

The Innsbruck Flow Drift Tube (IFDT) apparatus was used for the present investigation. It has been described in detail in the literature [8], thus only a brief outline of its main features needs to be given here. Ions were produced in a simple electron impact ion source operating with variable electron energy instead of hollow cathode discharge source. These ions enter the drift chamber through a small orifice of diameter 50 μm and through the helium, neon and argon buffer gas under the influence of an electric field towards the downstream end plate of the chamber, when part of the ions enter in the analyzing system (quadrupole mass spectrometry) through an orifice in the end plate. A constant flow of buffer gas through the drift tube is maintained at a small enough rate, so that the drift velocity of the ions is always high relative to the bulk flow velocity of the buffer gas through the drift section. Addition of chlorine gas (of research grade purity) to the buffer gas causes a decline of the count rate of reactant ions (and an increase of new produced ions) from which the rate coefficient of the reaction can be calculated in the usual way [8].

Measurements were performed at various E/N values, where E is the electric field strength and N the buffer gas density in the drift section. The mean relative kinetic energy KE_{rel} between the ions and the neutral chlorine Cl_2 was calculated using the Wanniers formula [9] in the usual way. Then according to [10] the KE_{rel} is expressed as:

$$KE_{cm} = \frac{M(m+M_i)}{2(M+M_i)} v_d^2 + \frac{3}{2} kT \quad (1)$$

where M , m and M_i are the masses of the reactant neutral (in our case Cl_2), of the buffer gas and of the reactant ions, respectively, v_d is the drift velocity of the reactant ions in the buffer gas, k is the Boltzmann constant and T is the neutral gas temperature (a room temperature).

Results and discussion

It is common that rate coefficients obtained in drift tube experiments are expressed as a function of KE_{cm} , derived using Eq.(1). Reaction rate coefficients obtained for the total destruction of N_2^+ , Ar^+ and Ar^{++} by reaction with chlorine Cl_2 as a function of KE_{cm} are shown in Fig. 1, Fig.2 and Fig.3, respectively for different buffer gas pressures.

The reaction of N_2^+ with Cl_2 has the large reaction rate coefficients. The remarkable changes of rate coefficients from $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ to $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ are observed in energy range from thermal up to a few eV KE_{cm} . The dominant reaction is



and for it only decline was observed, so indicating that vibrationally excited N_2^+ either reacts at the same rate as non-excited N_2^+ or that $\text{N}_2^+(X, v=0)$ is quenched faster (mainly in He buffer gas) than it does react with Cl_2 . Similar rate coefficients for both vibrationally excited and non excited N_2^+ could be expected in case of these two reactions, as both reactions are fast, even at room temperature and in general fast reactions hardly ever show a significant influence by the vibrational excitation of the ions.

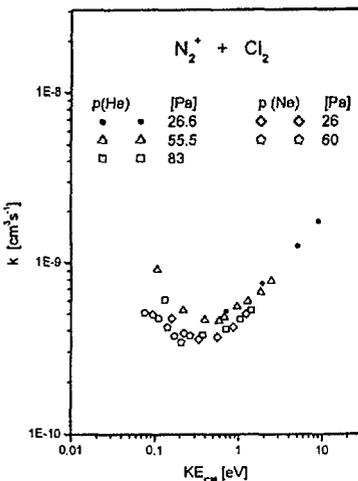


Fig.1: Rate coefficients k for the reactions of N_2^+ ions with Cl_2 in dependence on the relative mean kinetic energy KE_{cm}

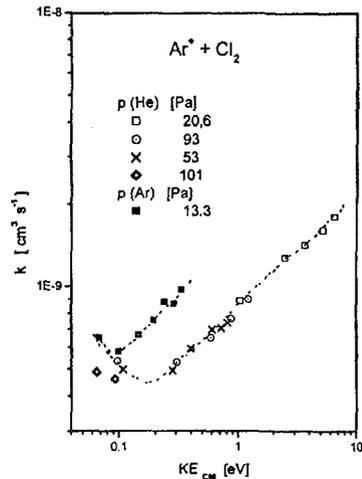


Fig. 2. Rate coefficients k for the reaction of Ar^+ ions with the Cl_2 in dependence on the relative mean kinetic energy KE_{cm}

There are three important and energetically possible reactions of Ar^+ ions with Cl_2 :



The branching ratio between reaction (3) and (4) was measured only for near thermal energy KE_{cm} . This ratio is similar to that observed by Lias [4] and R.S.Goodman [2]. The present results for total reaction rate coefficient of Ar^+ with Cl_2 shown in Fig.2 are about of one order higher than those presented by Lias. ($1.5 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$) [4].

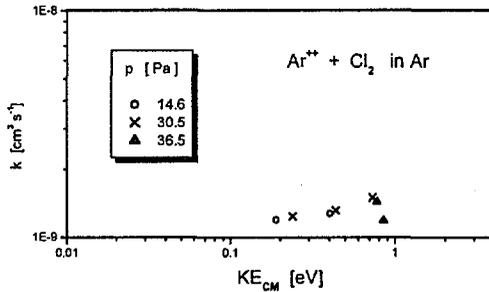


Fig. 3 Rate coefficients k for the reaction of Ar^+ ions with Cl_2 in argon in dependence on the mean relative kinetic energy

The reaction of doubly ionized argon ions Ar^{2+} with chlorine Cl_2 is important for excimer laser. It can be expressed as



with an exothermicity of about 13 eV.

Results of our measurements are presented in Fig. 3. It can be seen that this rate constant is of order $1 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ what is about 3 times higher than that ones ($4 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$) measured by I. Kuen with F. Howorka [11] and ($2.9 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$) by S.G. Lias [4].

Conclusions

We have shown that the N_2^+ , Ar^+ and Ar^{2+} positive ions react with chlorine Cl_2 very fast and that the corresponding reaction rate coefficients depends on the mean relative kinetic energy KE_{cm} . In the case of the reaction of Ar^+ with Cl_2 , its reaction coefficient depends also on the buffer gas. It can imply the enhancement of Cl_2^+ ions during etching of Si in the Ar/Cl_2 mixtures. The reaction of He^+ , Ne^+ and Kr^+ with chlorine Cl_2 has been also investigated. The results of these measurements will be published elsewhere [12].

Acknowledgement

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