Transport Coefficients in Mixtures Ar/H_2

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In this work we present electron transport coefficients for electrons in Ar/H_2 mixtures for the conditions used in plasma assisted technologies for semiconductor production i.e. in moderate to very high reduced electric field E/N (E — electric field, N — gas density). We used a two term numerical solution of the Boltzmann equation at the lowest E/N and mean energies and also Monte Carlo simulation technique at moderate and high E/N. We show that a good agreement with experimental data exists for low and moderate E/N and that based on the tests for pure H_2 and Ar we can model properly the high E/N development. Results were obtained for abundances of H_2 from 1% to 50%. Such data are required to test the sets of cross-section data which are necessary in kinetic models for this mixture and also to produce transport coefficients for fluid models. Hydrogen is used for etching of organic compounds, most importantly low k dielectrics, at the same time argon as a buffer gas is added to control the mean energy and distribution function. Besides, operation at high E/N allows the generation of fast neutrals for charging free etching on nanometer scales.

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1. Introduction

In a number of technologies argon is a typical buffer gas which allows control of electron temperature (mean energy may be quite high and one may support the selected processes with high threshold). Mixtures with hydrogen in rf plasmas may be useful for ashing of photoresists in microelectronic processing, but may also be used in a broader range of procedures.

In this paper we study the kinetics of electrons at E/N by using Monte Carlo simulations that have been well tested for similar discharges in Ar, H_2, and N_2. We focus on a special role that electrons have in plasmas and at high E/N discharges, leaving out heavy particle collisions which will be dealt with separately. Another motivation is to provide the transport data for the electrons in the mixtures of Ar and H_2 for modeling of such plasmas and also to point out the need to employ a more detailed kinetic modeling in sheath regions. These results can be used as the basis for modeling of anomalously broadened Doppler profiles which are particularly pronounced in Ar–H_2 mixtures [1], fast neutral plasma etchers for organic dielectrics and the whole range of plasma ashing/cleaning devices.

2. The Monte Carlo technique

A swarm is an ensemble of particles which move as a collective, do not interact mutually, and their motion is determined only by collisions with the atoms or molecules of the gas through which they move and the possibly present electric field. The behaviour of a swarm of electrons moving through a neutral gas can be described by transport coefficients. The basic transport coefficients are the drift velocity, the diffusion coefficient, the characteristic energy and the coefficients for ionisation and attachment.

Transport coefficients are measured for two reasons: because of possible direct use of these results in the analysis of experiments or modelling, and also because of the determination of the cross section for scattering.

Determination of cross-sections is a complex process consisting of several steps [2]. The first step is collecting sets of maximally precise experimental data (w — the drift velocity, eD_t/μ — the characteristic energy, the ionisation, excitation and coefficient of capture) for a wide range of E/N values. The range of cross-section energies to be covered depends on the width of the range E/N.

In the following step a test set of cross-sections is defined. One chooses a complete set of cross-sections for all processes which exist in the energy range from 0 eV to the energy 10 times higher than the maximum mean energy of the electrons. This set is based on the best possible results obtained in experiments with swarms or crossed beams, and in theoretical calculations. It is necessary to know the characteristics of the components, the energy limits of the cross-sections and which cross-sections are tied.

Transport coefficients are obtained by using a two term approximation (TTA) to the electron Boltzmann equation [3] and by Monte Carlo simulations [4, 5] (MCS). The TTA technique is very frequently used in plasma modeling in spite of its limited accuracy [6].

We use the argon cross-sections from our calculations for argon electron (and ion) swarms [7]. For hydrogen we use the data defined in the data base of Petrović and Phelps [8]. Both sets are based on accurate low energy cross-sections that were tested aginst the best swarm data at low E/N and have been tested against the emission profiles at high E/N and energy distribution functions. Thus there is no reason to question the application

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of such set for the mixture of two gases covering similar energies.

3. Discussion and results

In Fig. 1 we show the electron energy distribution function (EEDF) for the mixture of Ar and a small yet variable percentage of H_2 for the reduced electric field $E/N = 10$ Td. This example shows that the effect of hydrogen addition from 1% to 50% reduces number of electrons in 10 eV energy group by two orders of magnitude. The shape of the EEDF changes considerably and the highest energy electrons are depleted as hydrogen is added.

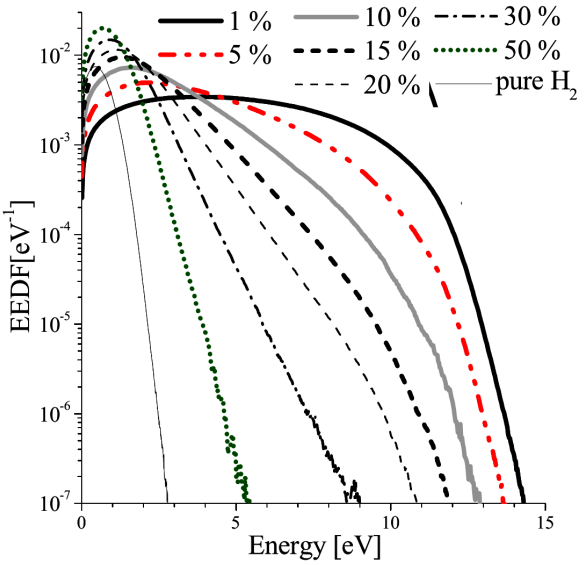

Fig. 1. EEDF obtained by MCS for a broad range of the Ar/H_2 mixtures where the parameter is taken as a percentage composition of hydrogen in the mixture.

Figure 2 shows electron drift velocity in the mixture Ar/H_2 as a function of E/N. Even a smallest addition of H_2 completely changes the shape of the drift velocity and induces effect of negative differential conductivity (NDC). The range of NDC is, however, reduced by a further increase of hydrogen concentration and is eventually lost beyond 15% of added hydrogen. In drift velocity plots we have also used the ELENDIF code [3] to calculate drift velocity at lower energies where the Monte Carlo simulation becomes inefficient (for higher H_2 abundances lower energies extend to higher E/N). Agreement with the experimental results of Engelhardt and Phelps [9] (EXP) confirms that a well-chosen set of sections is used to describe the behaviour of electrons in Ar/H_2 mixtures.

In Fig. 3 we show the mean energy of electrons in the mixture Ar/H_2 as a function of E/N. These results were obtained by the Monte Carlo code when H_2 is present from 1–20%.

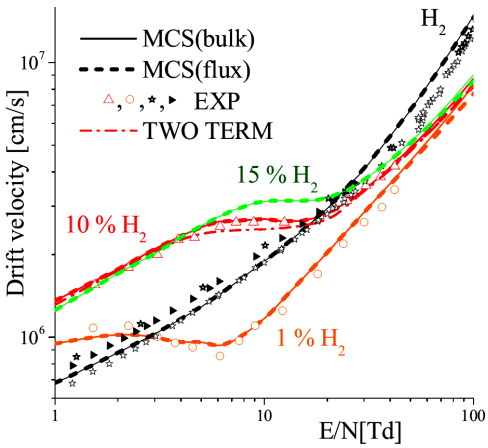

Fig. 2. Electron drift velocity for the mixture of Ar and H_2. Experimental values for pure H_2 are from Dutton [10].

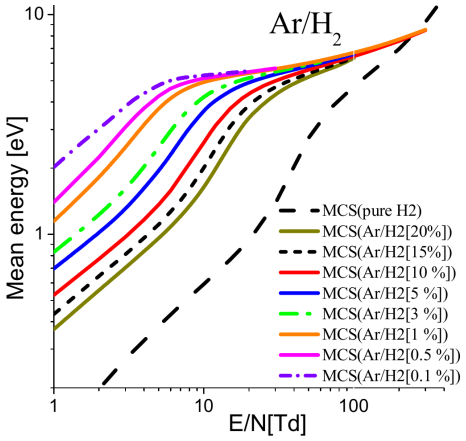

Fig. 3. Mean electron energy for the mixture of Ar and H_2.

There are notable changes in energy due to adding a secondary maximum hydrogen at lower E/N, where the influence of inelastic losses of electrons in collisions with hydrogen greatest.

The resulting transport coefficients are in agreement with existing experimental results, confirming that the effective scattering cross-section set which we have chosen can be used as a basis for modeling non-equilibrium conditions in the Ar/H_2 mixture gas discharges.

4. Conclusion

In this paper we show calculated electronic transport coefficients for the Ar/H_2 mixture under conditions where the dominant influence is exercised in the collisions of electrons with Ar and in conditions in which the influence of H_2 [11, 12] is significant. The resulting transport coefficients are in agreement with existing experimental results. We confirmed that the set of effective scattering

cross-section we have chosen can be used as a basis for modeling non-equilibrium regions in the gas discharges with Ar/H_2 mixture.

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