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SUPERELASTIC COLLISIONS IN SILANE DISCHARGES

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The aim of this paper is to show that superelastic collisions between electrons and vibrationally excited silane molecules may influence the kinetics of electrons in silane discharges. It was found that non-equilibrium vibrational temperature as large as 2000 K may be expected which increases significantly the rate of dissociation (and of other inelastic processes) as compared to the results for the gas in equilibrium at the room temperature.

1. Introduction

Most advances in development of plasma devices for the deposition of amorphous silicon have been achieved empirically, but in order to have a full understanding of the processes involved and to make further scientific and technological advances in this field a much better knowledge of the elementary processes in silane discharges is required. A large number of papers was recently published dealing with electron kinetics[1-3], gas-phase and surface processes[4,5] that lead to the thin film deposition. The starting point for all the gas-phase and surface chemistry is the dissociation of silane molecules by electron impact. Consequently, techniques for calculation of the dissociation rates should be reliable and reasonably accurate.

In the analysis of electron transport at moderate and high values of the reduced electric field (E/N), (where E is electric field and N is gas density). Superelastic collisions are usually omitted because: 1) they increase the complexity of the methods for solving Boltzmann equation (BE) for electron transport[6]; and 2) the energy gain in collisions with excited levels (normally rotational) becomes small as

compared to the average energy of electrons. However, it has been shown by Capitelli and his coworkers[7,8] that non-equilibrium population of excited vibrational levels (which are the result of the perturbation of gas by the flow of electric current) can reach such level that the energy gain in superelastic collisions affects the electron energy distribution function (EEDF). The aim of this paper is to show that superelastic collisions can influence significantly electron kinetics in silane discharges under certain working conditions which overlap with the conditions of some experimental and manufacturing devices[9,10].

2. *Numerical procedure*

In our calculations we have used a set of cross sections for silane developed by Ohmura et al.[3]. A two term solution[6] was calculated for the steady state Boltzmann equation

$$\frac{E^2}{3N}\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\left(\frac{\varepsilon}{\sigma_m(\varepsilon)}\frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\right)+\frac{2mNkT}{M}\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\left(\varepsilon^2\sigma_m(\varepsilon)\frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\right)+\frac{2mN}{M}\frac{\mathrm{d}}{\mathrm{d}\varepsilon}[\varepsilon^2\sigma_m(\varepsilon)f_0(\varepsilon)]+$$
$$+\sum_{j<k}N_j[(\varepsilon+\varepsilon_{jk})f_0(\varepsilon+\varepsilon_{jk})\sigma(jk;\ \varepsilon+\varepsilon_{jk})-\varepsilon f_0(\varepsilon)\sigma(jk;\varepsilon)]+$$
$$+\sum_{j<k}N_k[(\varepsilon+\varepsilon_{jk})f_0(\varepsilon+\varepsilon_{jk})\sigma(kj;\varepsilon-\varepsilon_{jk})-\varepsilon f_0(\varepsilon)\sigma(kj;\varepsilon)]=0 \qquad (1)$$

where

$$N_k=\frac{w_k}{w_j}N_j\,\mathrm{e}^{-\varepsilon_{jk}/kT};\quad \sigma(kj)=\frac{w_j}{w_k}\frac{\varepsilon}{\varepsilon-\varepsilon_{jk}}\sigma(jk),\quad \int_0^\infty\varepsilon^{1/2}f_0(\varepsilon)\,\mathrm{d}\varepsilon=1,$$

σ_m is the momentum transfer cross section, $\sigma(jk;\varepsilon)$ is the total cross section for inelastic collisions $j\to k$ with the energy loss ε_{jk}, $\sigma(kj;\varepsilon)$ is the cross section for the corresponding superelastic process, m and M are masses of electron and molecule and w_j is the statistical weight of the level j.

The corresponding rate and transport coefficients were then determined

$$v_{dr}=-\frac{eE}{3N}\left(\frac{2}{m}\right)^{1/2}\int_0^\infty\frac{\varepsilon}{\sigma_m(\varepsilon)}\frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\,\mathrm{d}\varepsilon \qquad (2)$$

$$\nu_{jk}=v_{dr}\left(\frac{\varepsilon}{N}\right)_{jk}=N\left(\frac{2}{m}\right)^{1/2}\int_0^\infty\varepsilon\sigma(jk;\varepsilon)f_0(\varepsilon)\,\mathrm{d}\varepsilon, \qquad (3)$$

where $\left(\frac{\varepsilon}{N}\right)$ is the excitation coefficient and ν_{jk} the collision frequency. Results are shown in Fig. 1—3 as full lines. As expected the agreement with the experimental data[11] used to produce the cross sections[3] is good, and only at higher values of E/N, D_T/μ values are in disagreement with the more recent data of Millican

and Walker[12] (compare full lines I and II in Fig. 2). A simplified model for the vibrational level kinetics was used to calculate the non-equilibrium populations represented by the effective vibrational temperature. Only the first excited levels

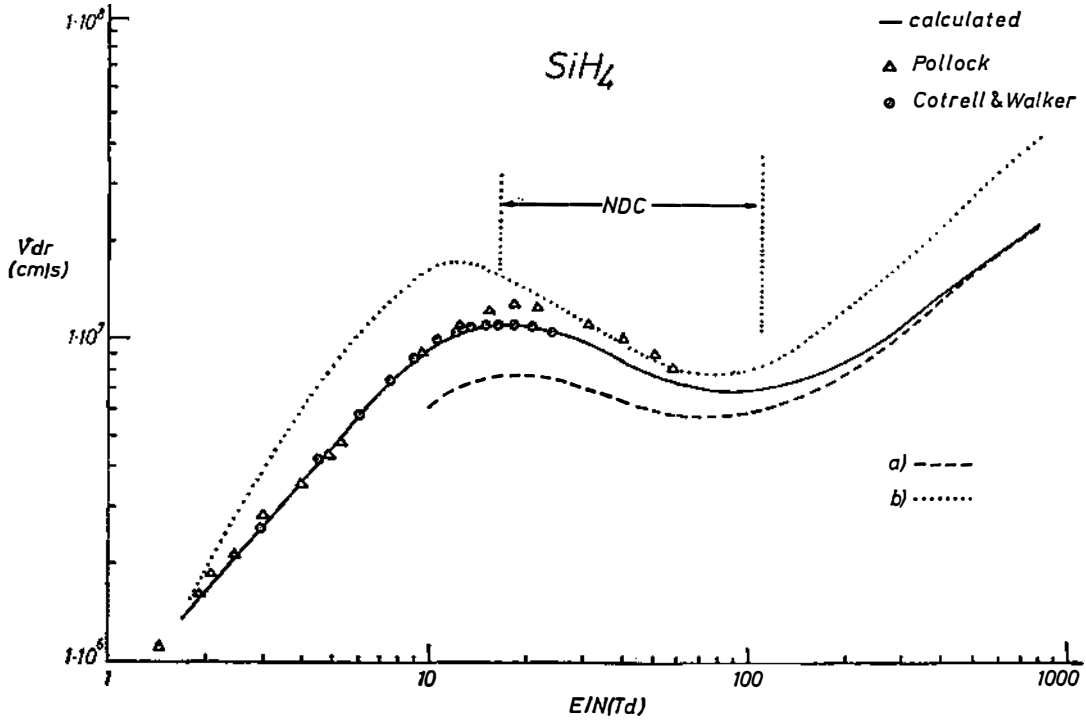

Fig. 1. Drift velocities of electrons in pure silane. Values calculated on the basis of the used cross sections are presented as a full line. Dashed line (a) shows the values calculated with the inclusion of superelastic with vibrationally excited silane (T_s = 2000 K). The dotted line (b) shows the effect on the calculated drift velocities of the assumption that vibrational excitation is purely forward scattering process. The region of negative differential conductivity is denoted by NDC and is clearly reduced when superelastic processes become more pronounced[5]. Available experimental data are given for comparison.

(four model lumped into two) were taken into consideration-thus a reasonable assumption has been made that the relaxation of the higher vibrational levels is faster than the corresponding excitation. V-R (vibrational-rotational) processes were neglected due to a high symmetry of the molecule. Rates of V-T (vibrational-translational) relaxation (and of the inverse process) and diffusion were determined on the basis of the available literature[13]. Coupling between two pairs of modes was neglected because any energy transfer between them would be non-resonant.

Therefore for a steady state discharge the concentration of molecules excited to the level v is:

$$[v] = \frac{\nu_{jk}\, nN}{\nu_{rel}\, N + D_v/\Lambda^2}$$

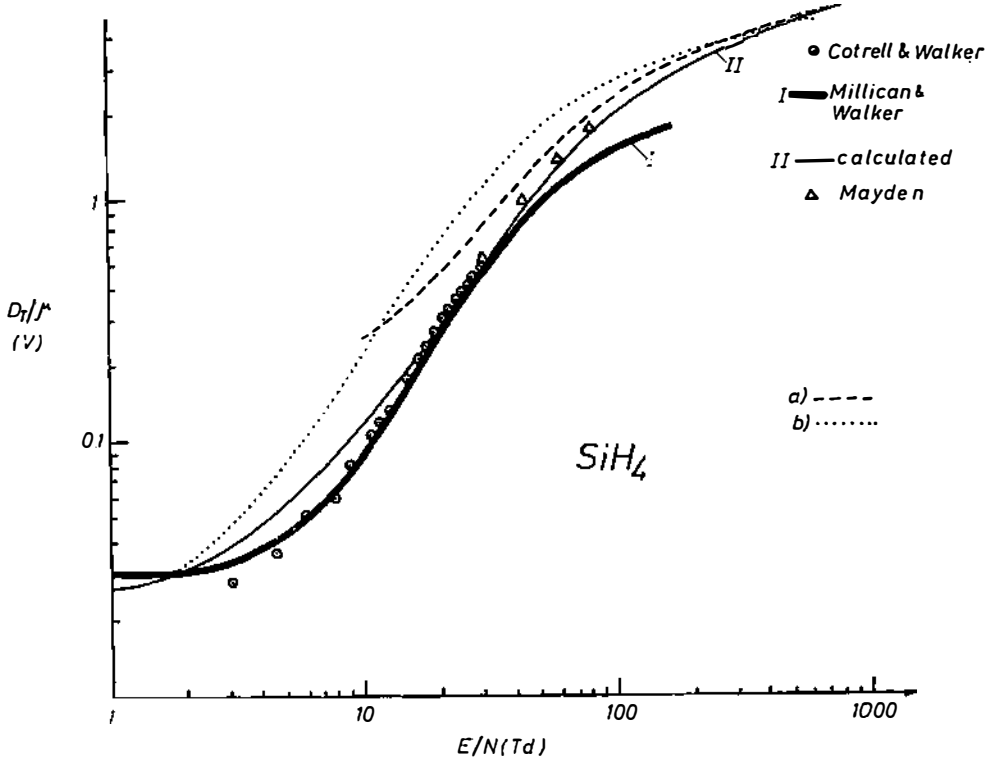

Fig. 2. D_T/μ values for electrons in pure silane. The notation is the same as in Fig. 1.

where

$$n = \frac{j}{e\, v_{dr}},$$

ν_{rel} is the vibrational relaxation collision frequency, D_v is the diffusion coefficient for the excited molecule Λ is the characteristic dimension of the cell (which can include effect of reflection[14] though in present calculations zero reflection has been assumed), and j is the electron current density.

3. *Results and discussion*

It was found that above 13 Pa and for current densities below 5 mA/cm^2 collisional relaxation is sufficiently fast to keep the vibrational temperature below 500 K but at lower pressure vibrational temperatures become quite large (depending on the size of the discharge tube). We have taken 2000 K to be the upper limit of the vibrational temperature for working conditions which can still be regarded as realistic for plasma processing. In the next step of the analysis BE was

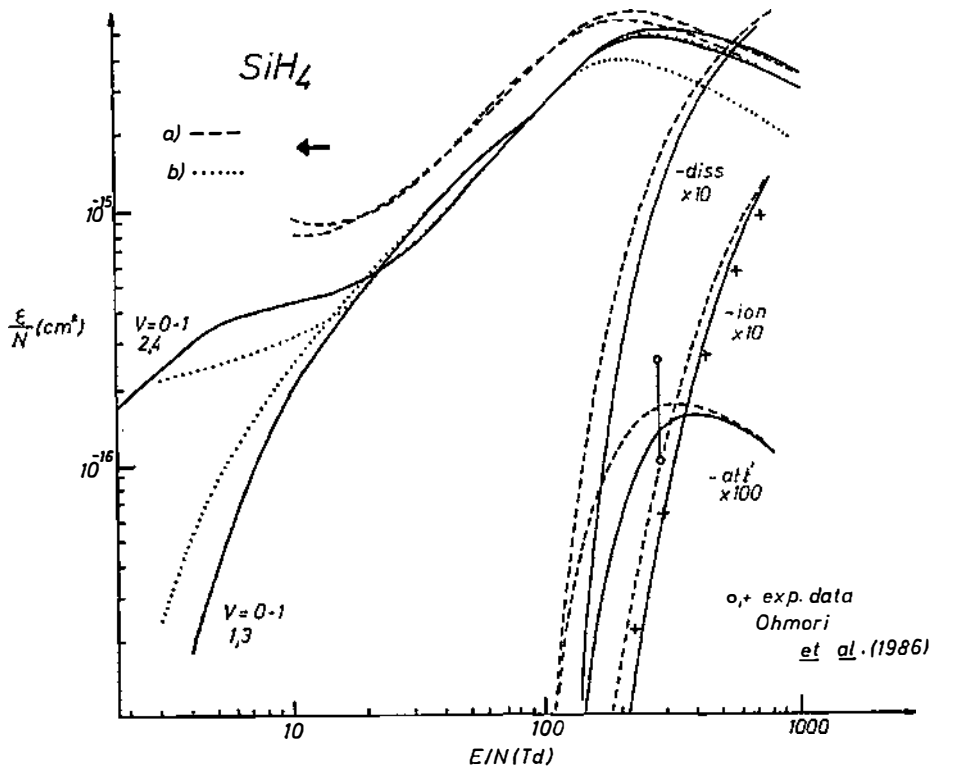

Fig. 3. Kinetic coefficients for various inelastic processes in pure silane: vibrational ($v = 0 - 1_{2,4}$) and $v = 0 - 1_{1,3}$) excitation, dissociation (diss), attachment (att) and ionization (ion). The notation is the same as Fig. 1. Experimental data for ionization and one example for attachment are also shown[3].

solved but the influence of the non-equilibrium vibrational population was taken into account.

First it was found that the rates of various processes were not changed appreciably by an increased percentage of excited molecules (30%) whose threshold energy for different inelastic collisions is somewhat reduced. This could be expected because the first vibrational excitation energy of SiH_4 is rather low (0.113 eV) and much smaller than the threshold energies for other inelastic processes. Such effect is expected to be quite important for Ar-SiH_4 mixtures where significant increase of the population of the argon metastable states could occur.

Non-equilibrium population of vibrational levels influences significantly the EEDF through superelastic collisions:

$$SiH_4\,(v = 1) + e\,(\varepsilon) \rightarrow SiH_4\,(v = 0) + e\,(\varepsilon + \Delta\varepsilon). \qquad (1)$$

In Fig. 4 are shown the EEDF when such process is included (a) in comparison with the calculation for the gas in equilibrium (b). As can be seen, the high energy

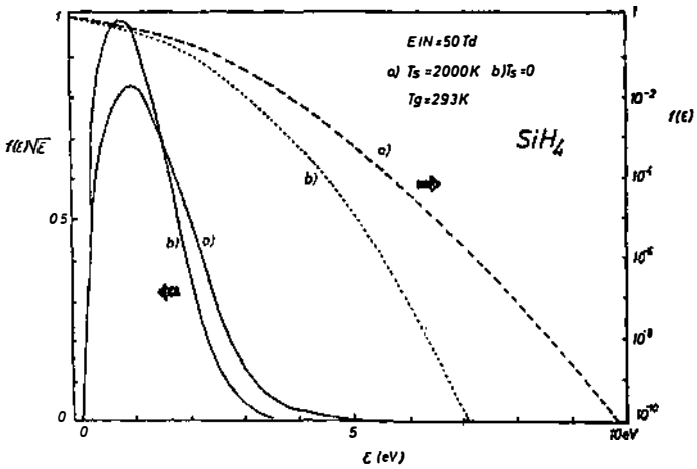

Fig 4. Electron energy, distribution functions $f(\varepsilon)$ and $f(\varepsilon)\sqrt{\varepsilon}$ in relative units in pure silane at 50 Td:

a) superelastic collisions included ($T_s = 2000$ K)

b) unperturbed gas ($T_s = 293$ K).

tail of the EEDF is several orders of magnitude larger when superelastic collisions are included. This makes a large impact especially on the calculated rates of inelastic processes with high thresholds calculated on the basis of such EEDF (see Fig. 3 - dashed lines).

Other transport data are also quite different (see dashed lines in Figs. 1—3) from the calculated and experimental data for the unperturbed gas.

At higher values of E/N influence of superelastic collisions becomes smaller in proportion to the ratio between the superelastic energy gain and the average energy of electrons. However, the E/N range which is usually encountered in applications and experiments with pure silane, the superelastic collisions still make a significant contribution to the energy balance of electrons and the dissociation rate can be increased by a factor of 3—5.

Full self-consistent calculations were not performed but the final effect is expected to be even larger. First order calculation was considered sufficient to prove the point. There are no difficulties to extend the calculation further and it should be done for specific systems if accurate results are required.

In present calculations it was assumed that inelastic collisions are isotropic according to the model or Ohmura et al.[3]. However, in the region of the Ramsauer--Townsend minimum, inelastic cross sections are larger than the eleastic momentum transfer cross section. For these energies results should be strongly dependent on the angular distribution of the inelastic differential cross section. In order to illustrate the magnitude of the possible effects of non-isotropic vibrational excitation cross section, we have performed a calculation (for the unperturbed gas) where all the inelastic cross sections were assumed to be dominantly in forward direction (no contribution to the momentum transfer cross section) and these results are shown by dots in Figs. 1—3).

We should also note that the behaviour of the drift velocity versus E/N, which shows the negative differential conductivity (NDC), is in full agreement with the recently developed explanations of the phenomenon of NDC[15].

4. *Conclusion*

Most studies of complicated reaction schemes in silane discharges depend on accurate calculations of the dissociation rate coefficients. For the working conditions of some of these experiments it is clear that superelastic collisions with vibrationally excited molecules should be included in the analysis. Uncertainty in these calculations comes from the lack of data for relaxation and excitation of higher vibrational levels and for accomodation coefficients. Nevertheless a reasonably accurate, simplified model can be constructed for certain conditions.

The aim of this paper was not to present the accurate data for any specific system but just to indicate the importance of taking into account superelastic collisions with the nonequilibrium population of vibrationally excited silane molecules. Therefore we have used the Boltzmann equation for the d. c. electric field (which is directly relevant to a limited number of experimental studies[9]). In R. F. fields some new effects are expected to take place[16], but even in that case the conclusions of this paper would still be valid. For the time dependent fields superelastic collisions will affect the rate of temporal relaxation of the EEDF[8] thus making it even more important to take these processes into account.

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SUPERELASTIČNI SUDARI U PRAŽNJENJIMA U SILANU

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Originalan naučni rad

Cilj ovog rada je da pokaže da superelastični sudari elektrona sa vibraciono pobuđenim molekulima silana mogu da utiču na kinetiku elektrona u gasnim pražnjenjima kroz silan. Ustanovljeno je da se u određenim uslovima mogu očekivati neravnotežne vibracione temperature čak i do 2000 K, što znatno povećava brzinu disocijacije (i ostalih neelastičnih procesa) u odnosu na rezultate koji se dobijaju za gas u termodinamičkoj ravnoteži na sobnoj temperaturi.