Hydrogen Discharge Diluted with Argon: A Global Model Study

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Introduction

- Hydrogen plasmas play an important role in various fields of science and technology such as in thermonuclear fusion, astrophysics and materials processing
- Negative hydrogen ion sources are needed to produce intense neutral beams for injection into next-generation magnetically confined fusion reactors
- Applications of low pressure high density hydrogen plasmas in materials processing include
  - plasma immersion ion implantation (PIII)
  - hydrogenation

Introduction

- High densities of H and H^+ particles are desired for efficient hydrogenation
- The dissociation energy of molecular hydrogen is 4.52 eV
- The vibrationally excited hydrogen molecule $H_2(v > 0)$ plays an important role in dissociation and ionization processes in the plasma volume
- The electron affinity of atomic hydrogen is 0.75 eV and the threshold for dissociative attachment is 3.75 eV at $v = 0$ and decreases to values below 1 eV for $v > 6$
- The hydrogen discharge is generally considered weakly electronegative

Outline

- The global (volume averaged) model
  - Basic equations
  - Model parameters
- Comparison with measurements
- Particle densities
  - Electronegativity – the role of vibrationally excited levels
  - Creation and destruction of H^-, H_3^+, and ArH^+
- Summary

The global (volume averaged) model

The global (volume averaged) model

- A steady state global (volume averaged) model was developed for the H_2/Ar discharge
- The following species are included
  - electrons
  - the ground state atoms and molecules: H, Ar, H_2
  - the vibrationally excited hydrogen molecules: $H_2(v = 1 - 14)$
  - the negative hydrogen ion H^-
  - the positive ions H^+, H_2^+, H_3^+, Ar^+
  - electronically excited arogn atoms metastables (Ar^m ($1s_5$ and $1s_3$)), radiatively coupled states (Ar^r ($1s_4$ and $1s_2$)) and Ar(4*p*)
- The content of the chamber is assumed to be nearly spatially uniform and the power is deposited uniformly into the plasma bulk

Hjartarson et al. *Plasma Sources Sci. Technol.*, **19** 065008 (2010)

The global (volume averaged) model

- The particle balance equation for a species X is given

$$\frac{\mathrm{d}n^{(X)}}{\mathrm{d}t} = 0 = \sum_i R^{(X)}_{\mathrm{Generation},i} - \sum_i R^{(X)}_{\mathrm{Loss},i}$$

  where $R^{(X)}_{\mathrm{Generation},i}$ and $R^{(X)}_{\mathrm{Loss},i}$, respectively, are the reaction rates of the various generation and loss processes of the species X

- The power balance equation, which equates the absorbed power P_{abs} to power losses due to elastic and inelastic collisions and losses due to charged particle flow to the walls is given as

$$\frac{1}{V}\left[P_{\mathrm{abs}} - eVn_{\mathrm{e}}\sum_{\alpha} n^{(\alpha)}\mathcal{E}^{(\alpha)}_{\mathrm{c}}k^{(\alpha)}_{\mathrm{iz}} - eu_{\mathrm{B0}}n_{\mathrm{i}}A_{\mathrm{eff}}(\mathcal{E}_{\mathrm{i}} + \mathcal{E}_{\mathrm{e}})\right] = 0$$

The global (volume averaged) model

- For the edge-to-center positive ion density ratio we use

$$h_L \simeq \left[\left(\frac{0.86}{(3 + \eta L/2\lambda_\mathrm{i})^{1/2}} \frac{1}{1+\alpha_0} \right)^2 + h_\mathrm{c}^2 \right]^{1/2}$$

$$h_R \simeq \left[\left(\frac{0.8}{(4 + \eta R/\lambda_\mathrm{i})^{1/2}} \frac{1}{1+\alpha_0} \right)^2 + h_\mathrm{c}^2 \right]^{1/2}$$

where $\alpha_0 \approx (3/2)\alpha$ is the central electronegativity, $\eta = 2T_+/(T_+ + T_-)$ and

$$h_\mathrm{c} \simeq \left[\gamma_-^{1/2} + \gamma_+^{1/2} [n_*^{1/2} n_+ / n_-^{3/2}] \right]^{-1} \quad \text{and} \quad n_* = \frac{15}{56} \frac{\eta^2}{k_\mathrm{rec} \lambda_\mathrm{i}} v_\mathrm{i}$$

is based on a one-region flat topped electronegative profile

$$\gamma_- = \mathrm{T_e/T_-} \quad \text{and} \quad \gamma_+ = \mathrm{T_e/T_+}$$

Kim et al., J. Vac. Sci. Technol. A, **24** 2025 (2006)

The global (volume averaged) model

- The diffusional losses of the neutral hydrogen atoms to the reactor walls are given by

$$k_{\mathrm{H,wall}} = \left[\frac{\Lambda_{\mathrm{H}}^2}{D_{\mathrm{H}}} + \frac{2V(2-\gamma_{\mathrm{rec}})}{Av_{\mathrm{H}}\gamma_{\mathrm{rec}}} \right]^{-1} \quad \mathrm{s}^{-1}$$

  - D_{H} is the diffusion coefficient for neutral hydrogen atoms
  - $v_{\mathrm{Cl}} = (8eT_{\mathrm{g}}/\pi m_{\mathrm{H}})^{1/2}$ is the mean H velocity
  - γ_{rec} is the wall recombination coefficient for neutral hydrogen atoms on the wall surface
  - Λ_{H} is the effective diffusion length of neutral hydrogen atoms

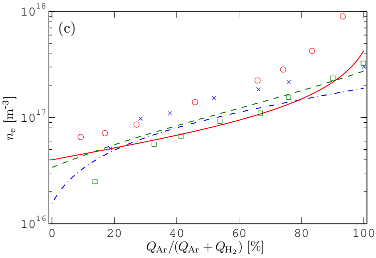
$$\Lambda_{\mathrm{Cl}} = \left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2 \right]^{-1/2}$$

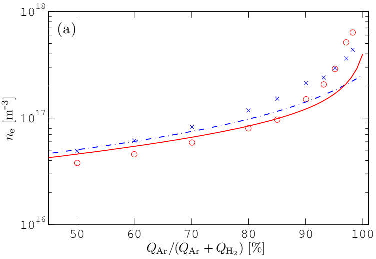
- We use a wall recombination coefficient $\gamma_{\mathrm{rec}} = 0.023$

Curley et al., J. Vac. Sci. Technol. A, **28** 360 (2010)

Comparison with experiments

Comparison with experiments–Electron density





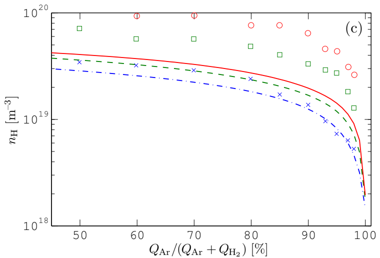
- ICP anodized aluminum chamber
- $L = 7.62$ cm and $R = 15.24$ cm
- x 2, □ 7 and ○ 30 mTorr and $P_{\text{abs}} = 600$ W

Gudmundsson, *Plasma Sources Sci. Technol.*, **7** 330 (1998)

- ICP stainless steel chamber
- $L = 7.5$ cm and $R = 8$ cm
- x 20, and □ 40 mTorr and $P_{\text{abs}} = 120$ W

Kimura and Kasugai, *J. Appl. Phys.*, **107** 083308 (2010)

Comparison with experiments–Atomic hydrogen density



- ICP stainless steel chamber
- $L = 7.5$ cm and $R = 8$ cm
- x 20, □ 40 mTorr, and ○ 60 mTorr and $P_{abs} = 120$ W

Kimura and Kasugai, *J. Appl. Phys.*, **107** 083308 (2010)

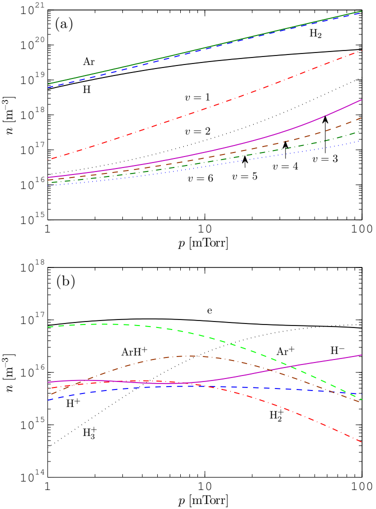
- The measured atomic hydrogen concentration compared to the model calculations
- At 40 and 60 mTorr the density of atomic hydrogen is measured to be somewhat greater than the model implies but at 20 mTorr there is good agreement

Particle densities

Particle densities

- The role of the vibrationally excited molecules increases with increased gas pressure
- The Ar^{+}-ion dominates below 10 mTorr and the H_3^{+}-ion above 10 mTorr
- a cylindrical aluminum chamber
  radius $R = 15.24$ cm
  length $L = 7.62$ cm

  $P_{abs} = 600$ W and 50 % H_2/50 % Ar



Electronegativity

- The negative ion H^- is almost entirely produced by dissociative attachment

$$e + H_2(v) \longrightarrow H + H^-$$

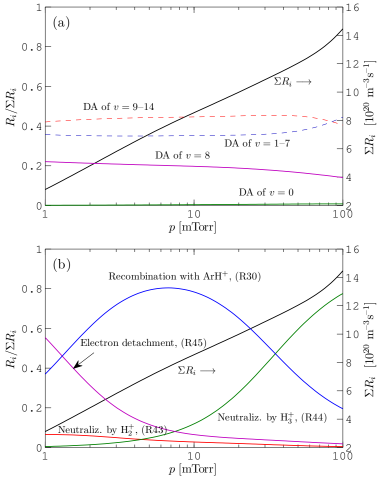
- The negative ion H^- is mainly lost through ion-ion recombination

$$H^- + ArH^+ \longrightarrow H_2 + Ar$$

up to 36 mTorr pressure

- a cylindrical aluminum chamber
radius $R = 15.24$ cm
length $L = 7.62$ cm

$P_{abs} = 600$ W and 50 % H_2/50 % Ar



Electronegativity

- At higher pressures the mutual neutralization

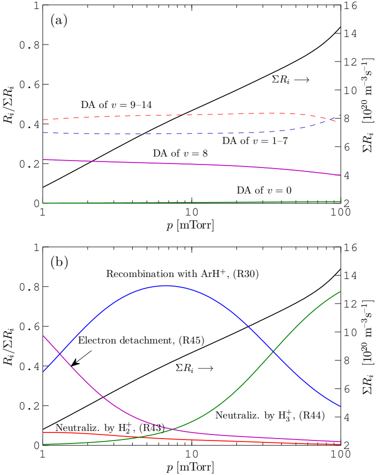
$$H_3^+ + H^- \longrightarrow 4H$$

dominates and at low pressures

$$e + H^- \longrightarrow H + e + e$$

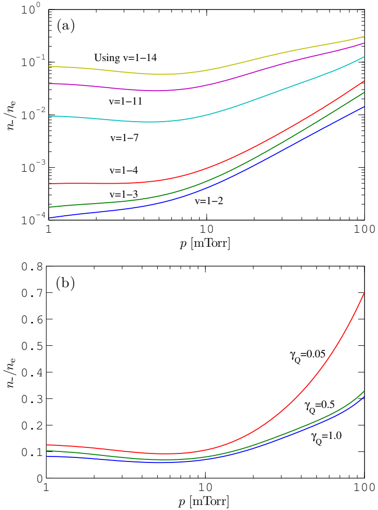
is important

- a cylindrical aluminum chamber
  radius $R = 15.24$ cm
  length $L = 7.62$ cm
  $P_{abs} = 600$ W and 50 % H_2/50 % Ar



Electronegativity

- The electronegativity is low
  - decreases with increased argon dilution
  - increases with increased discharge pressure
- The cross section for dissociative attachment increases and the threshold decreases with vibrational excitation
- Dissociative attachment from the $v = 7 - 9$ states contributes roughly 50 % to the creation of H^-



H_3^+-ion

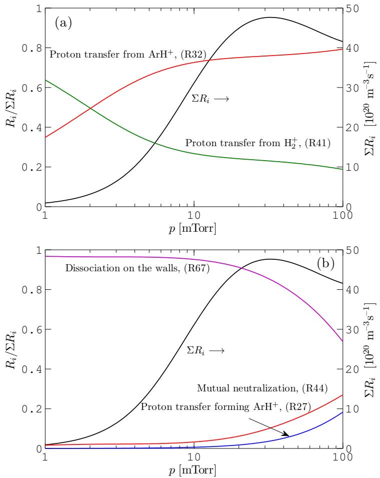
- Creation of H_3^+ is through

$$H_2 + ArH^+ \longrightarrow H_3^+ + Ar$$

$$H_2 + H_2^+ \longrightarrow H + H_3^+$$

- The loss of H_3^+ is dominated by dissociation at the walls
- The ion ArH^+ is very important
- a cylindrical aluminum chamber
  radius $R = 15.24$ cm
  length $L = 7.62$ cm

  $P_{abs} = 600$ W and 50 % H_2/50 % Ar



ArH^+-ion

- The atom transfer reaction

$$H_2 + Ar^+ \longrightarrow H + ArH^+$$

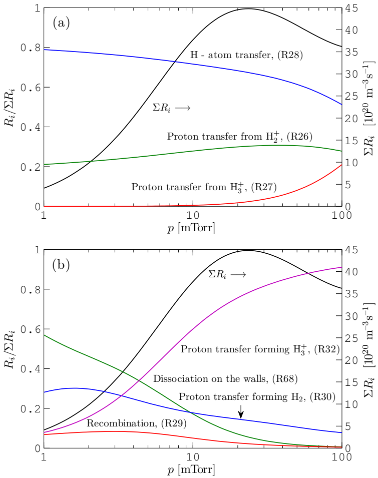
is most effictive in the creation of ArH^+

- The loss is dominated by dissociation at the walls and the proton transfer reaction

$$H_2 + ArH^+ \longrightarrow H_3^+ + Ar$$

- a cylindrical aluminum chamber
  radius $R = 15.24$ cm
  length $L = 7.62$ cm

  $P_{abs} = 600$ W and 50 % H_2/50 % Ar



Summary

Summary

- A global model of a H_2/Ar discharge has been developed for the pressure range 1–100mTorr
- Dissociative attachment from the $v = 7 - 9$ states contributes the most to the creation of H^- or about 50 %
- The influence of argon dilution was explored and in particular the role of the ion ArH^+
- The density of the ArH^+-ion is significant, in particular in the pressure range 2–30 mTorr, and it plays a crucial role in the destruction of the H^--ion in this pressure range