Diffusion of Sputtered Ground-State Tungsten Atoms in Krypton

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Abstract. The work is dedicated to investigations of the diffusive transport of sputtered ground-state tungsten atoms in buffer gas krypton at ambient temperatures. For sputtering of the metal, a pulse-periodic longitudinal hollow cathode gas discharge in cylindrical geometry is used. The cathode represents a 20 cm in length and 2.6 cm in diameter hollow copper cylinder, the inner surface of which is coated with a thin tungsten layer. During the discharge W atoms are sputtered from that layer into the cathode volume, while in the afterglow phase their density decreases due to diffusive losses back to the surface. The diffusive loss rates are measured by using a time-resolved double-channel optical absorption technique. By relating the experimental loss rates with a diffusion model based on the experimental geometry and a boundary condition of the third kind, the following value for the diffusion coefficient of W atoms in krypton is obtained: $D_0 = 130_{-30}^{+40}$ cm$^2$s$^{-1}$ at 133 Pa buffer gas pressure and 315 K temperature. The reflection coefficient of these atoms at the cathode surface is obtained within the range $0 \leq \rho \leq 0.8$. The experimental results for the diffusion coefficient are compared with theoretical calculations based on model interaction potentials.

1. Introduction

Transport properties of metal atoms in gases are a subject of scientific interest [1-5] due to the wide application of metal vapours in various plasma devices for layer deposition, lighting, etc. The subject of the investigations starting with this work is the diffusive transport of sputtered ground-state tungsten atoms in rare gases. Namely, the diffusion coefficients in the bulk and the reflection coefficients (or the complementary sticking probabilities) of these atoms at a solid cathode surface with mixed composition at temperatures around ambient are to be studied.

The method for simultaneous determination of the absolute values of ground-state metal atoms’ diffusion coefficients in the gas phase and reflection coefficients at a surface is considered in detail elsewhere [6-8]. It is based on the dependence of the gas phase particles’ diffusion losses on the drain rate at the wall. In brief it can be described as follows. Material sputtering in gas discharge is a convenient way of producing atomized metal-gas mixtures at ambient and elevated temperatures. We usually use pulse-periodic hollow cathode gas discharges in cylindrical geometry (Figure 1). During the pulse metal atoms are sputtered from the internal walls of the hollow cathode inside the volume. In the afterglow period, the metal density decreases due to diffusive losses towards the walls of the cathode. An optical-absorption technique with time resolution is applied to record the decay curves of
the ground-state metal atoms’ density in the cathode, using the absorption of a resonance line. A suitable external source of atomic linear spectra is the hollow cathode discharge lamp.

The experimental decay curves are compared with appropriate solutions of the diffusion equation, which are dependent on two parameters, namely the diffusion coefficient and the sticking probability of the metal atoms to the cathode wall surface. The diffusion equation for an infinite in length cylinder of radius \( R \) is solved by using the boundary condition of the 3-rd kind [6]:

\[
\frac{N(R)}{\varepsilon} = -\frac{dN}{dr} \bigg|_{r = R},
\]

where \( \varepsilon = 0.71\lambda \frac{1 + \rho}{1 - \rho} \) is the so-called linear extrapolation length. Here \( N \) is the diffusing atoms number-density, \( \lambda = \frac{3D}{\nu} \) is their mean free path, \( D \) is the diffusion coefficient, \( \nu \) is the mean thermal velocity, \( r = R \) is the wall position. The quantity \( \rho \) is the reflection coefficient of the atoms at the wall, which is the probability that the gas phase atoms impinging on the surface are scattered back into the volume. It is related with the sticking coefficient \( s \) by the expression \( \rho = 1 - s \).

The boundary condition (1) implies a non-zero density at the wall. We can assume that the density becomes zero at some distance further behind the wall on the so-called extrapolated wall with radius \( R^* \). Then, the solution of the diffusion equation for the late afterglow (when all higher order diffusion modes have decayed away) can be built with a zero boundary condition at \( r = R^* \), as given by:

\[
N(r,t) \propto J_0 \left( \mu_i \frac{r}{R^*} \right) \exp \left[ -D \frac{\mu_i^2}{R^*^2} t \right].
\]

Here \( J_0 \) is the zero-th order Bessel function, \( \mu_i \) is its first root, \( R^* \) is the extrapolated radius. The substitution of (2) in (1) gives the necessary relationship between \( R^* \) and the rest of the parameters, which scales the actual distribution inside the cylinder:

\[
\frac{J_0(\mu_i^*)}{J_1(\mu_i^*)} = \mu_i^* \frac{2D}{\nu} \left[ \frac{1 + \rho}{1 - \rho} \right]; \quad \mu_i^* = \mu_i \frac{R^*}{R}.
\]

The logarithm of (2) is a linear function of time with a slope \( S \),

\[
S = -D \frac{\mu_i^2}{R^*^2}.
\]

The decay rate \( |S| \) depends on both \( D \) and \( \rho \), since \( \mu_i^* \) is an implicit function of these two parameters. If such a plot is taken from the experiment, then \( |S| \) is a known quantity. Obviously a single-valued solution for both parameters \( D \) and \( \rho \) can be derived by using at least two linearly independent relations of this type. They can be obtained in two ways: by varying the buffer gas pressure or the tube radius. This procedure provides simultaneous determination of both parameters.

The method can be applied for other simple geometries—spherical or plane-parallel—by using the appropriate solutions [6]. It does not require precise absolute measurements of the species densities, since the decay rate is the basic necessary experimental output.

2. Experimental

The experimental setup is given schematically in Figure 1. Two discharge tubes operated in pulse-periodic mode are used. The absorption tube contains a cathode that represents a 20 cm in length and
2.6 cm in diameter hollow copper cylinder, the inner surface of which is coated with tungsten sheet. The typical discharge conditions for the absorption tube are: krypton gas pressure 20–100 Pa, pulse duration 1–2 ms, pulse current 100–250 mA, pulse voltage 600V. The emission tube is filled with krypton as well and contains a small hollow cathode plated with tungsten (22 mm in length and 11 mm in diameter). It is operated with short discharge pulses (200–400 μs duration and 60–100mA current). Both discharges are synchronized, working with a pulse period in the range 20–30 ms. The light from the emission tube is passed through the absorption tube and the 75-cm Czerny-Turner monochromator selects the resonance W I 2551 line. The optical signal is registered by the photomultiplier (PMT) working in photon-counting mode. The time resolution of the measurements is achieved by gating the PMT output. Two gate pulses with controlled delays are generated by the experiment controller, realizing the so-called double-channel setup. For each time point in the afterglow four optical fluxes are measured. They are used to calculate the relative absorption of the resonance line emitted during the emission tube discharge pulse in the absorption tube volume.

**Figure 1.** Experimental setup.

**Figure 2.** Portions of the emission tube spectrum and Hg reference spectrum in the UV region around W I 2551 line.
The relative absorption is measured automatically in successive steps covering portions of the absorption tube afterglow. Assuming Doppler broadening of the absorption and emission line profiles at the working temperature and literature data for the line strength, the absorption time dependencies are converted into ground-state ($^3$D$_0$) W atoms’ decay curves.

A portion of the emission tube UV spectrum around the W resonance line, together with a reference Hg spectrum is given in Figure 2. Both spectra are recorded simultaneously by operating the emission cathode and an external reference Hg lamp inserted in the optical scheme, with multiplexed in time pulses. They are aligned with the two measurement channels, which gate the PMT output, so that each channel measures a separate spectrum.

3. Results and discussion

Figure 3 contains two decay curves of the W ground-state atoms’ density for 26 and 94 Pa krypton pressure. The logarithmic plot shows linear behaviour with respect to time in the early portions of the afterglow which indicates, as expected, an exponential decay of the W atoms’ density. Based on the experimental decay rates, calculated from these curves, the value for the diffusion coefficient, normalized for 133 Pa (1 Torr) gas pressure has been obtained: $D_0 = 130^{+40}_{-30} \text{ cm}^2\text{s}^{-1}$ at 315 K temperature. The reflection coefficient value is found within the range: $0 \leq \rho \leq 0.8$.

According to the kinetic theory of Chapman and Enskog [1], the diffusion coefficient for binary mixtures $D_{12}$ can be obtained if the interaction potential between the particles is known:

$$D_{12} = \frac{3}{16} \sqrt{\frac{2\pi kT}{p\pi\sigma_{12}^3\Omega(T,\varepsilon)}},$$

where $\mu$ is the reduced mass of the two collision partners, $p$ and $T$ are the gas pressure and absolute temperature, $\sigma_{12}$ is the inter-atomic distance at which the potential energy is zero, $\Omega(T,\varepsilon)$ is the collision integral which is dependent on the interaction potential.

If such a potential is not available, estimations are often made by implementing model potentials. In this work we have tried the rigid spheres model and the Lenard-Jones 12–6 potential by using data for the atomic radius (130 pm for W and 198 pm for Kr) and potential well depth $\varepsilon$ (0.59 eV for W and
0.018 eV for Kr) taken from [1]. The results for 315K temperature and 133 Pa pressure are: rigid spheres model, \(D_0=97 \text{ cm}^2\text{s}^{-1}\); Lenard-Jones 12–6 potential, \(D_0=34 \text{ cm}^2\text{s}^{-1}\).

Due to the deep potential well for W, both models give results, which differ from each other almost 3 times. Both are lower than the experimental value. The rigid sphere model, however, gives a value, which is close to the uncertainty range of the experimental result.

The accuracy of the experimental results depends on several factors, including the initial level of the absorption signal and hence, the maximum density of W atoms achievable in the sputtering discharges. Tungsten has low sputtering yields and in our experimental conditions the maximum registered absorption in the initial phase of the afterglow was around 10%. Under the current experimental conditions the value of the diffusion coefficient is determined with accuracy better than that of the reflection coefficient. To decrease the reflection coefficient uncertainty, lower pressures and smaller cathode diameters have to be used.

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