Transport properties of ground-state aluminium atoms in hollow cathode gas discharge plasma

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Abstract. For investigation of Al atoms transport properties a pulse-periodic longitudinal hollow cathode gas discharge in cylindrical geometry is used. The cathode represents a 20 cm in length and 1.8 cm in inner diameter hollow aluminium cylinder. During the discharge Al atoms are sputtered from the wall into the cathode volume, while in the afterglow phase their concentration decreases due to diffusive losses back to the wall surface. The diffusive loss rates at different buffer gas pressures are measured by using a double-channel time-resolved optical absorption technique with gated photon counting. By relating the experimental loss rates with a diffusion model based on the experimental geometry and a boundary condition of the third kind, the diffusion coefficient of ground-state Al atoms in argon, as well as the reflection coefficient of these atoms from the cathode surface are obtained. The experimental value for the diffusion coefficient at 313 K temperature and 133 Pa argon pressure is $D_0 = 160 \pm 30 \text{ cm}^2\text{s}^{-1}$. The reflection coefficient was found to be in the range: $0.2 < \rho < 0.82$. The result for the diffusion coefficient is compared with theoretical results based on 12-6 Lenard-Jones and rigid-sphere inter-atomic interaction model.

1. Introduction

Vapours of aluminium atoms are generated by sputtering, or thermal evaporation in various layer deposition systems, Al spectral lamps, lasers, etc [1, 2]. Filling rare gases in a wide range of pressures are used in many of these devices. The performance of the latter, whether in stationary or pulsed mode of operation, is dependent on the transport behaviour of the metal atoms. This work is a continuation of a series of our previous works [3, 4] dealing with transport properties of metal atoms. It is focused on determination of the diffusion coefficient of ground-state ($3p^2\;^2P_{1/2}$) aluminium atoms in argon at ambient temperatures.

Diffusion coefficients of metal atoms in gases can be obtained by several experimental techniques. Stefan’s method applies evaporation of the metal in an oven under well-controlled temperature, geometry and boundary conditions with measurement of the mass loss for a given time interval. Other methods are based on measurements of the spatial density distribution (stationary or non-stationary conditions), or density decay rates in non-stationary cases. To retrieve the diffusion coefficient, the results from these measurement techniques are related to appropriate solutions of the diffusion equation. In our experiments we work in non-stationary conditions. Sputtering by pulse-periodic gas discharge in cylindrical hollow cathode is used to create sufficient amount of Al atoms inside the cathode volume during the pulse. The only process in the discharge afterglow that leads to loss of
metal atoms in the volume is diffusion and sticking to the walls. The atoms' density decay in the afterglow is detected and tracked by an optical-absorption technique based on a double tube scheme. For absorption measurements involving ground-state aluminium atoms, some authors have also used diode lasers [1, 2]. The temporal evolution of Al atoms density in the hollow cathode is dependent on their diffusion coefficient and also on their reflection coefficient from the cathode wall. This parameter is generally unknown beforehand and has to be taken into account for the specific experimental conditions. This is usually done through selection of the boundary condition. We use a method for simultaneous determination of the diffusion coefficient of particles in gases and their reflection coefficient from the wall of the container, described in details in [3], which implements a boundary condition of the third kind.

2. Experimental
The experimental setup is similar to those used in previous works [4]. Figure 1 gives a general description. The absorption discharge tube is made of pyrex glass. It contains a 20 cm in length and 1.8 cm in inner diameter cylindrical aluminium hollow cathode. The cathode is placed in an additional glass tube, preventing the discharge from spreading over the outer cathode surface. The anode is a small cylinder placed at one side of the absorption tube, close to the edge of the cathode. The absorption tube is filled with argon at various pressures between 20 and 200 Pa. The tube is covered with isolating polyurethane foam and the working gas temperature is measured by a mercury thermometer placed in contact with the glass wall. The emission tube contains a 18 mm in length and 12 mm in inner diameter cylindrical aluminium hollow cathode and is filled with argon as well. Both tubes are operated in synchronized pulse-periodic mode, which is provided by the experiment controller and the double-channel pulsed high voltage supply. The typical periods of pulse repetition are chosen in the range 20 – 30 ms. The absorption tube pulses (widths in the range 1-1.5 ms) are modulated to provide more efficient sputtering of the cathode. The average current during the absorption tube discharge pulse is in the range 100 – 200 mA. The emission tube discharge current is 50 – 70 mA and its duration — typically 150 – 300 µs. All windows and lenses along the optical path are made of fused silica, providing transmission of ultraviolet light.

The discharge in the emission tube is a source of linear atomic spectrum of aluminium. This light passes through the absorption tube volume, where the resonance line (Al I 3082), connected with the ground-state level is partially absorbed. The resonance line is selected by the 75-cm Czerny-Turner monochromator and detected by the photomultiplier tube (PMT). The latter works in photon-counting mode. The PMT output pulses coming at a rate proportional to the input light flux are gated and counted by the experiment controller. Gated counting provides measurements of the relative
absorption of the resonance line in the absorption tube volume with time resolution. Figure 2 shows the measurement scheme in its double-channel arrangement. Two separate channels (gate pulses G1 and G2 with equal duration, typically 100 – 300 µs, gating two separate counters) are positioned in the afterglow period. Gate G1 is placed at the current point of measurement. Gate G2 is fixed in the late afterglow for reference measurement. Both tubes are operated continuously in pulsed mode, which provides temperature stability. During a predefined dwell time interval, the delay of the emission pulse alternates periodically between two positions, corresponding to alignment with G1 or G2. Counts from both channels are separately collected for each of these phases of measurement. This provides measurement of four fluxes, including background, with sufficient statistics. Besides, effects of possible long-term drifts of PMT gain or the emission tube brightness are compensated. Based on the measured fluxes, the relative absorption is calculated. The relative absorption is automatically measured in successive steps by changing G1 delay. In this way selected portions of the afterglow are scanned.

The recorded absorption time dependencies are converted into decay curves of ground-state Al (\(^2\)P\(_{1/2}\)) atoms’ density by using literature data for the line strength (0.18) [5] and hyperfine structure of the resonance Al I 3082 line, emitted in the transition 3d \(^2\)D\(_{3/2}\) – 3p \(^2\)P\(_{1/2}\) [6]. The hyperfine structure is used to calculate the emission and absorption line profiles at the working temperature, assuming Doppler broadening of the line components. Natural aluminium is represented 100 percent by the single stable isotope \(^{27}\)Al, which has a nuclear spin of 5/2. The combination of atomic shell moments in the upper and lower states of the transition with the nuclear spin gives 6 hyperfine components of the emitted line. Figure 3 shows an illustration of the line profile calculated for 310 K. The centre of gravity of the line is indicated by zero on the horizontal axis.

Figure 4 shows a portion of the emission tube spectrum, scanned with the 75-cm monochromator at 0.1 mm slit widths. The Al doublet (wavelengths 308.2 and 309.3 nm), containing the analytical line can be seen.

Figure 2. Double-channel measurement scheme with gated photon counting.
3. Results and discussion
Decay curves have been measured at different argon pressures in the absorption tube. Figure 5 shows a set of such curves, already converted into metal atoms’ density time dependencies. The maximum value of the relative absorption achieved in the experiments is around 40%, which corresponds to $3 \times 10^{10}$ cm$^{-3}$ atoms’ density. The detection limit depends on the line strength, absorption path length, level of averaging of measured optical fluxes, precision of zeroing possible baseline offsets. For the presented experimental conditions it is around $1 \times 10^9$ cm$^{-3}$ (1 – 2% absorption signal). The decay curves shown in figure 5 in semi-logarithmic plot are recorded some time after the end of the discharge pulse to allow decay of higher order diffusion modes. They are linear with time before getting too close to the detection limit. This corresponds to an exponential decay of aluminium atoms’ density, as expected in the diffusion model. From the linear portions corresponding decay rates (respectively effective lifetimes) are obtained. Figure 6 shows the lifetime versus buffer gas pressure dependence. Based on these results, the procedure for simultaneous determination of the diffusion coefficient of Al ($^3P_{1/2}$) atoms in argon and their reflection coefficient from the cathode wall is applied.

Figure 3. Calculated Doppler broadened profile of Al I 3082 line. T=310K.

Figure 4. Emission tube spectrum including the analytical line.
It consists in solving a system of equations, each one containing as parameters the diffusion and reflection coefficient, pressure and the corresponding to that pressure experimental effective lifetime. The following value for the diffusion coefficient $D_0$ normalized for 133 Pa argon pressure at 313 K temperature is obtained: $D_0 = 160 \pm 30 \, \text{cm}^2\text{s}^{-1}$. The combined uncertainty of the result includes contributions from pressure, cathode radius and experimental lifetime measurement uncertainties. The reflection coefficient $\rho$ is found in the range $0.2 < \rho < 0.82$.

The experimental value of the diffusion coefficient can be used to verify theoretical models of the inter-atomic interaction potential for the couple Al-Ar. According to the Chapman-Enskog theory, the diffusion coefficient $D_{12}$ of particles of sort 1 in a scattering gas medium containing particles of sort 2 is a function of the interaction potential between these particles [7]:

![Figure 5.](image1)

**Figure 5.** Experimental decay curves of ground-state Al atoms’ density at various argon pressures. $T=313$K.

![Figure 6.](image2)

**Figure 6.** Experimental diffusion lifetimes obtained from curves given in figure 5.
$D_{12} = \frac{3}{16} \sqrt{\frac{\mu}{p \pi \sigma_{12}^2 \Omega(T, e) \sqrt{2\pi(kT)^3}}}$, \hspace{1cm} (1)

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, $\Omega(T, e)$ is the collision integral which is dependent on the interaction potential. For comparison with the experiment, we have used here the rigid spheres model and the Lenard-Jones 12–6 potential. The rigid spheres approximation is the simplest model of interaction which is based on the definition of atomic radius. The latter, however, may vary since it can be defined in different ways. For example the empirical radius is estimated as the half of the inter-atomic distance in crystals, while a calculated radius can be obtained as the radius of the maximum charge density of the electron shell. The model gives a fixed interaction cross-section, independent of temperature, unlike the Lenard-Jones potential, which is characterized by two parameters: the inter-atomic distance at which the potential energy is zero $\sigma$ and the potential well depth parameter. The latter potential is generally considered as more realistic with regard to temperature dependencies of the diffusion coefficient. We made our estimations based on literature data for the atomic radii and potential well depths $\varepsilon$, taken from [7]. The results for 313K temperature and 133 Pa pressure are: rigid spheres model, $D_0 = 175$ cm$^2$s$^{-1}$; Lenard-Jones 12–6 potential, $D_0 = 110$ cm$^2$s$^{-1}$. The experimental result obtained in the present work lies between these two values and is closer to the rigid spheres result.

4. Conclusion

The diffusion coefficient of ground-state Al ($^2P_{1/2}$) atoms in argon at 313 K temperature was obtained by measuring the effective lifetimes of these atoms sputtered in a cylindrical hollow cathode at various argon pressures. The result was compared with two models of inter-atomic interaction. The value was closer to the rigid spheres result for the working temperature. The reflection coefficient of Al atoms at the cathode wall was estimated from the experimental measurements, being in the range between 20 and 82 %.

References

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