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Plasma diagnostics and modeling of lithium-containing plasmas

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Abstract

Thin-film deposition from chemically reactive multi-component plasmas is complex, and the lack of electron collision cross-sections for even the most common metalorganic precursors and their fragments complicates their modeling based on fundamental plasma physics. This study focuses on understanding the plasma physics and chemistry in argon (Ar) plasmas containing lithium bis(trimethylsilyl) amide used to deposit Li_xSi_y thin films. These films are emerging as potential solid electrolytes for lithium-ion batteries, and the Li-to-Si ratio is a crucial parameter to enhance their ionic conductivity. We deposited Li_xSi_y films in an axial flow-through plasma reactor and studied the factors that determine the variation of the Li-to-Si ratio in films deposited at various points on a substrate spanning the entire reactor axis. While the Li-to-Si ratio is 1:2 in the precursor, the Li-to-Si ratio is as high as 3:1 in films deposited near the plasma entrance and decreases to 1:1 for films deposited downstream. Optical emission from the plasma is dominated by Li emission near the entrance, but Li emission disappears downstream, which we attribute to the complete consumption of the precursor. We hypothesized that the axially decreasing precursor concentration affects the electron energy distribution function in a way that causes different dissociation efficiencies for the production of Li and Si. We used Li line intensities to estimate the local precursor concentration and Ar line ratios to estimate the local reduced electric field to test this hypothesis. This analysis suggests that the mean electron energy increases along the reactor axis with decreasing precursor concentration. The decreasing Li-to-Si ratio with axially decreasing precursor concentration may be explained by Li release from the precursor having lower threshold energy than Si release.

Keywords: plasma, lithium, solid electrolyte, silicon, battery, optical emission, electron energy distribution

(Some figures may appear in color only in the online journal)

1. Introduction

Plasma enhanced chemical vapor deposition (PECVD) is widely used to synthesize thin films at low temperature and

low pressure [1–5]. Independently controlled process variables, such as power, pressure, and gas composition, determine the internal plasma variables, such as the electron temperature, electron density, and species fluxes to various surfaces, which in turn affect the composition and properties of the films deposited via PECVD [1, 6, 7]. Understanding interrelations between these various quantities informs process parameter

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choices so that particle fluxes, surface reactions, and film properties can be controlled rationally [8, 9].

Thin Li_xSi_y films find applications in energy storage [10] and have attracted attention as the negative electrode material in lithium-ion batteries because of their large theoretical capacity [11–13]. A large Li-to-Si ratio in these films leads to high ionic conductivity [14] and is an important parameter that must be controlled to optimize battery performance. Many reports discuss electrochemical methods for depositing Li_xSi_y films [15, 16], but to our knowledge, there are no previous reports on PECVD of Li_xSi_y solid electrolyte thin films. In this study, we use a low-pressure nonthermal Ar plasma containing small concentrations of lithium bis(trimethylsilyl) amide (LiHMDS) to deposit Li_xSi_y thin films and explore the factors that affect the Li-to-Si ratio. Films were characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and x-ray photoelectron spectroscopy (XPS) to determine their composition and using SEM to determine their thickness. Optical emission spectroscopy (OES) in conjunction with line intensity ratio analysis was employed as a plasma diagnostic to estimate the electron energy distribution function (EEDF) at different axial positions. Local precursor concentrations were derived from the Li resonant line emission analysis. Li-to-Si ratios were interpreted based on Boltzmann calculations using tentative guesses for the unknown cross-sections of the LiHMDS precursor.

This paper aims to demonstrate that Li_xSi_y thin films can be deposited with PECVD and discuss the challenges associated with this approach. This may inform potential applications of this deposition approach for lithium-ion battery technologies.

2. Film deposition and characterization

Li_xSi_y films were deposited in the tubular capacitively coupled plasma deposition reactor shown schematically in figure 1(a). Figure 1(b) is a digital photograph of the plasma taken during deposition. The plasma was maintained in a 2.54 cm diameter 25.4 cm long cylindrical quartz tube by powering two 2 cm $\times$ 3 cm copper plates placed parallel on opposite sides of the quartz tube. The electrodes span 2–5 cm in the axial position, measured from the reactor inlet flange. One of the copper plates was powered by a 13.56 MHz radiofrequency (RF) sinusoidal wave (generated by amplifying ENI RF power amplifier model A150), amplifying a waveform from a function generator (Tektronix AFG 3251). Films were deposited on 1 cm wide 10 cm long rectangular strips cut from molybdenum foil and attached to the inner wall of the tubes on the side of the grounded electrode. This long strip allowed us to study the variation of the Li-to-Si ratio in the films as a function of axial position. Gases were fed from the top of the tube and pumped through the exhaust at the bottom using a mechanical pump (Trivac D16B). A bubbler filled with LiHMDS was connected to a sidearm near the top of the tube and maintained at 70 °C using a heater. LiHMDS sublimates at 70 °C generating LiHMDS vapor which was carried into the plasma using Ar as the carrier gas. Supplementary Ar gas, in addition to the carrier,

was fed from the top of the tube. Ar flow rates through both gas lines were maintained at 20 sccm each, yielding a total Ar flow rate of 40 sccm. The partial pressure of LiHMDS was determined from the pressure rise and was 10 mTorr. The total pressure during deposition was 340 mTorr. Typical conditions used in this study are listed in table 1. The substrates were cleaned for 10 min by maintaining a pristine Ar plasma before each deposition. Deposition duration was 10 min for each experiment, and the thicknesses of the films were determined from the SEM images.

The films were characterized using XPS (SSX-100, Surface Science), ICP-AES (Thermo Scientific iCAP 6500), and SEM (JEOL 6500). XPS was used to determine the atomic composition of the surface, while ICP-AES was used to characterize the film composition in the films. These measurements were conducted on 1 cm $\times$ 1 cm samples cut from the substrate at 1 cm, 3 cm, and 6 cm downstream from the reactor inlet. The XPS measurements were performed on a system equipped with a monochromated Al K_α x-ray source, a hemispherical sector analyzer, and a resistive anode detector. The film compositions (at.%) were calculated from the survey spectra using the ESCA HAWK software provided with the XPS system. For high-resolution data, the lowest binding-energy C 1s peak was set at 285.0 eV and used as the reference for all other elements. For ICP-AES, Li_xSi_y films were digested in hydrochloric acid. The solution was analyzed using a Thermo Scientific X series 2 ICP-AES equipped with an ESI PC3 Peltier-cooled spray chamber, SC-FAST injection loop, and SC-4 autosampler.

Figures 2(a)–(c) show the SEM images of films deposited at different axial positions while thicknesses obtained from these SEMs are plotted in figure 2(d) along with the Li-to-Si ratio obtained from both the XPS and the ICP-AES measurements. SEM results indicate that the films are smooth and highly dense. The thickest films (1.6–1.8 μm) are found in the upstream region (figure 2(a)), and the film thickness decreases downstream of the electrodes. Films in figures 2(a) and (b) were deposited within the plasma, while the film in figure 2(c) was deposited outside the intense plasma region. The Li-to-Si ratio was a strong function of axial position as shown in figure 2(d), changing approximately from 3:1 at the upstream edge of the substrate ($z = 1$ cm) to 1:1 at the downstream end ($z = 6$ cm). Materials characterization beyond $z = 6$ cm was not performed. However, one might expect that the Li-to-Si ratio decreases further downstream. This is surprising because the precursor contains two Si atoms per Li atom, and naïve reasoning would suggest a Li-to-Si ratio of around 1:2 should be expected in the films. Using a simple model described below, we explored the possible reasons for the axial variation of the Li-to-Si ratio in the films. This model provided insight into the factors that govern the Li-to-Si ratio in the films.

3. OES

OES was used to gain insight into the important plasma species that may give rise to the variation of the Li-to-Si ratio observed in figure 2. Optical emission at several axial locations was

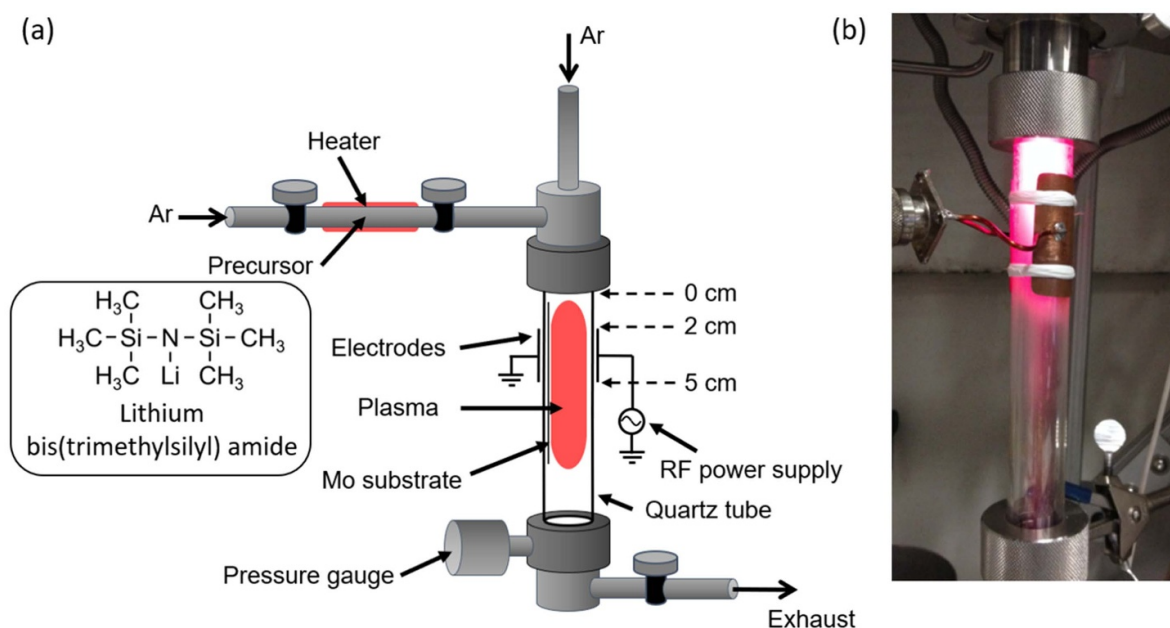


Figure 1. (a) A schematic of the plasma deposition reactor used in this study. (b) A digital photograph of the lithium- and silicon-containing Ar plasma generated by exciting LiHMDS vapor diluted in Ar gas.

Table 1. Typical plasma operating conditions.

Total flow rate	40 sccm
Ar flow rate	20 sccm
Ar + Li precursor	20 sccm
Precursor temp.	70 °C
Precursor %	3%
Pressure	340 mTorr
RF power	10 W
Deposition time	10 min
Substrate	Mo strip

imaged onto the entrance slit of a monochromator (SpectraPro 275 Action Research Corporation with a 1200 grooves mm^{-1} grating, entrance and exit slit set to 30 μm) using a lens coupled to a fiber optic cable. The distance between the lens and the quartz tube was maintained at 5 mm using a rail-guided holder while the axial location was adjusted smoothly. The emission was dispersed using the monochromator and detected using a Hamamatsu R3809U-50 microchannel plate photomultiplier tube and a Hamamatsu C5410 photo counter. The spectral resolution was approximately 0.33 nm.

To account for the spectral response of the SpectraPro 275 system and the quantum efficiency of the R3809U-50 photomultiplier, which peaks at 430 nm and strongly decreases in the red wavelength range, the spectrometer was cross-calibrated against an Avantes Avaspec USL2048CL-EVO that had been intensity calibrated with an Ocean Optics HL-3P-INT-CAL-EXT intensity calibration light source. This intensity calibration was used to convert raw optical emission data to relative spectral line intensities.

Figure 3 shows optical emission spectra at three different axial locations. The distances are measured from the reactor

tube inlet (0 cm). The top edges of the two parallel electrodes were 2 cm downstream of the inlet. An intense plasma extends from the electrodes to the inlet due to the coupling of the electric field to the metal flange (figure 1(a)). The optical emission at this position is entirely dominated by the Li 2p-2s transition at 670.8 nm and the Li 3d-2p transition at 610.4 nm. Even though Li represents only a very small fraction of the total gas mixture, as shown below in section 4, the Li lines exceed the strong Ar 4s-4p transitions between 690 and 800 nm by more than a factor of 20. This is not surprising, given that the excitation threshold energy of the 2p level in Li is only 1.85 eV and thus significantly below the excitation threshold of the prominent Ar lines. At 5 cm, between the electrodes, the Li 2p-2s transition is still the strongest emission, but the Ar 4p-4s transitions have increased significantly in intensity, and the Ar 5p-4s transitions around 400–450 nm have also gained in intensity. This suggests that a significant fraction of the precursor has been dissociated. Finally, at 8 cm, 2 cm downstream of the bottom edges of the parallel electrodes, Li emission has virtually disappeared, and the emission is now dominated by the strong Ar 4p-4s lines. This suggests that the LiHMDS precursor has been nearly completely consumed. We do not observe any of the expected strong Si emission lines at 288 nm and 252 nm, suggesting that the concentration of atomic Si in the plasma is low. Low Si concentration, in turn, suggests that Si must be bound to other atoms or possibly to one or more methyl groups.

The molecular fragments and atoms produced upon dissociation of the precursor are expected to affect the EEDF. To understand the variation of the plasma properties along the discharge, we measured the intensities of various Ar emission lines as a function of position and estimated the EEDFs and the associated reduced electric fields from the emission-line ratios, as discussed in section 4. The emission lines we used are listed

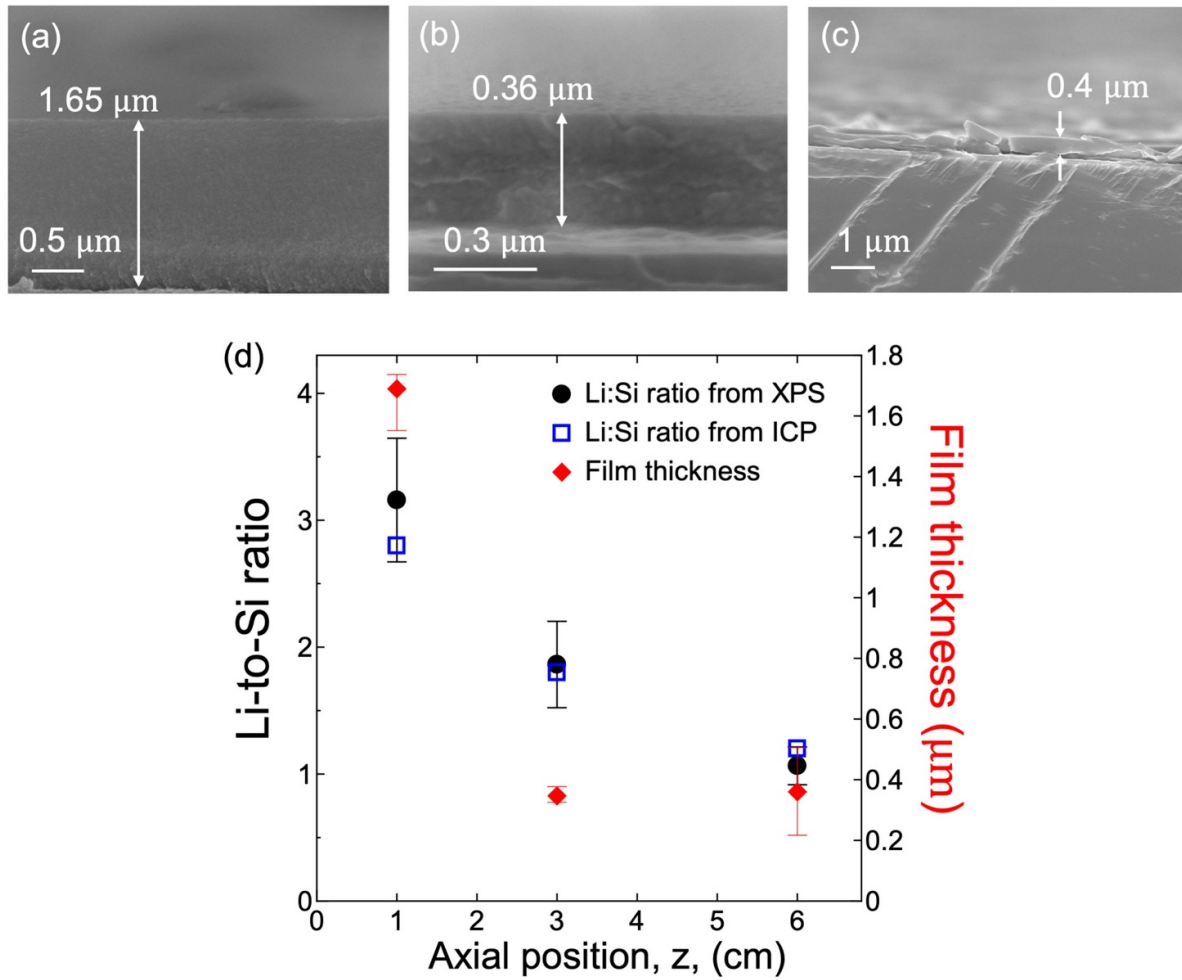


Figure 2. SEM images of films deposited at three different axial positions, specifically at, (a) $z = 1$ cm, (b) $z = 3$ cm and (c) $z = 6$ cm where $z = 0$ is the top of the quartz tube. (d) Film thickness and Li-to-Si ratio in the films as a function of axial position from the tube inlet. The Li-to-Si ratio determined by XPS and ICP-AES are both shown and agree with each other. The film was deposited under the conditions listed in table 1.

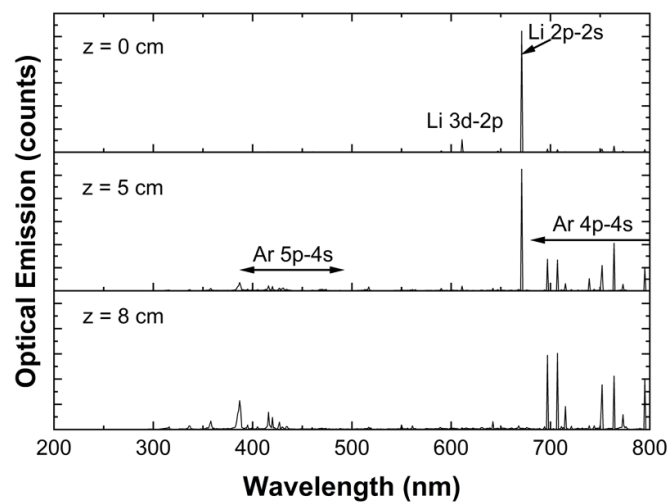


Figure 3. Optical emission spectra (raw data, not corrected for spectrometer spectral response) of the Ar-LiHMDS plasma at different axial positions. (a) $z = 0$ cm, at the reactor inlet and upstream of the electrodes, (b) $z = 5$ cm, between the electrodes, and (c) $z = 8$ cm, 2 cm downstream of the electrodes. Conditions are listed in table 1.

Table 2. A list of Ar emission lines used for estimating the EEDF. Here, λ is the wavelength, E_i is the threshold energy of the excitation to the upper level from the Ar ground state, A_i is the transition probability, and $A_i/\sum A_j$ is the branching ratio of the transition. All data are from the NIST Atomic Spectra Database [17].

λ (nm)	Transition	E_i (eV)	A_i (s^{-1})	$A_i/\sum A_j$
763.51	4p[3/2] ₂ –4s[3/2] ₂	13.17	2.45×10^7	0.71
751.46	4p[1/2] ₀ –4s[3/2] ₁	13.27	4.0×10^7	~ 1.0
750.39	4p'[1/2] ₀ –4s'[1/2] ₁	13.49	4.5×10^7	~ 1.0
419.83/420.07	5p[5/2] ₃ –4s[3/2] ₂ /5p[1/2] ₀ –4s[1/2] ₁	14.50/14.58	$2.57 \times 10^6/9.5 \times 10^5$	0.685/0.469
415.85	5p[3/2] ₂ –4s[3/2] ₂	14.53	1.4×10^6	0.816

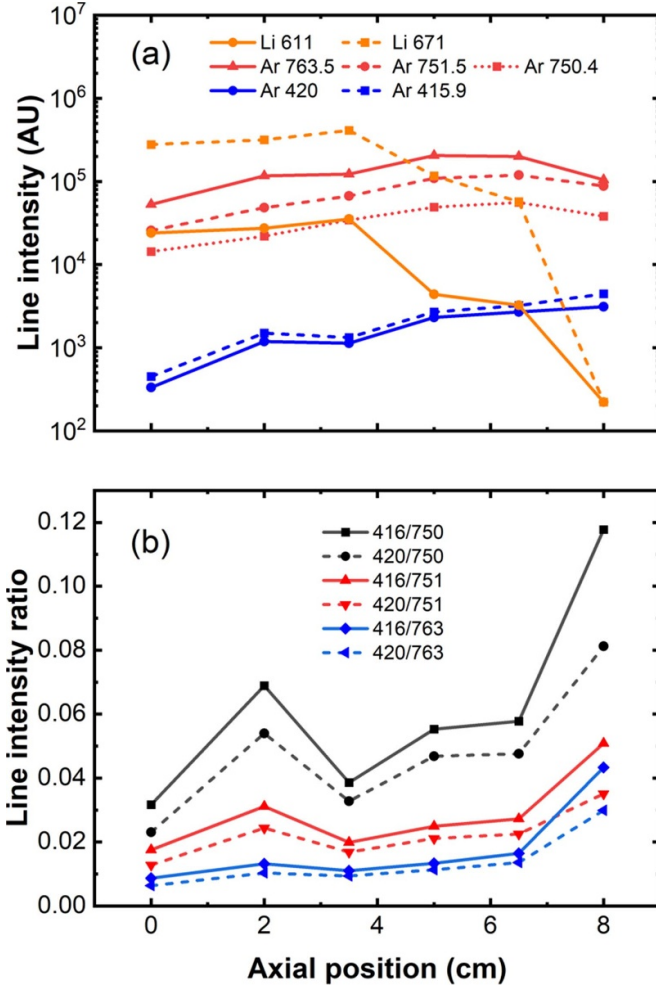


Figure 4. (a) Axial variation of Ar and Li emission line intensities in an Ar-LiHMDS plasma for the operating conditions listed in table 1. (b) Various Ar emission line intensity ratios as a function of axial position in the reactor.

in table 2. The two emissions at 419.83 nm and 420.07 nm are listed together because they were not resolved.

Figure 4(a) shows the axial variation of the Ar line intensities, along with those of the Li lines. The general trend is that as the Li line intensities decrease, reflecting the decrease of the precursor concentration along the axis, the Ar line intensities increase; the Ar 5p–4s lines with threshold energies around 14.5 eV increase faster than the Ar 4p–4s lines with threshold energies around 13.3 eV. This is reflected by

the general increases of the intensity ratios of all Ar 5p–4s/4p–4s line ratios, figure 4(b), which suggests an increase in the excitation temperature of the EEDF in that energy range.

4. Estimating the precursor concentration along the axial direction

To account for the influence of LiHMDS and its fragments on the plasma, we estimated their local concentrations along the discharge axis. The concentrations were calculated using a simple mass balance on the differential control volume shown schematically in figure 5. At steady-state, a constant flux of the precursor enters the control volume, and a smaller flux leaves due to dissociation of the precursor into Li and other fragments. Based on the strong Li emission observed, we assume that the dissociation of one precursor molecule ultimately results in one Li atom, possibly after multiple collision processes. At steady-state, the loss of Li via diffusion to the reactor walls is equal to the amount of Li produced by dissociation so that

$$(C_{p,z} - C_{p,z+dz})Au = C_{Li}dV/\tau_{diff} \quad (1)$$

where C_p and C_{Li} are the precursor and the Li concentrations, respectively, A is the cross-sectional tube area, u is the radially averaged gas velocity and $dV = Adz$. The diffusion time constant is calculated using $\tau_{diff} = D_{Li,Ar}/\Lambda_{diff}^2$, where $D_{Li,Ar}$ is the diffusion coefficient of Li in Ar, $\Lambda_{diff} = R/2.405$ is the diffusion length, and R is the tube radius. Equation (1) can be rearranged to

$$\frac{dC_p}{dz} = -\frac{C_{Li}}{u\tau_{diff}}, \quad (2)$$

and then integrated from the reactor entrance at $z = 0$ to $z = L = 8$ cm, assuming that $C_p(0) = C_{p,0}$ is the initial precursor concentration at the entrance and that $C_p(L) = 0$. We define a dimensionless function $0 \leq f(z) \leq 1$ and write C_{Li} as $C_{Li}(z) = C_{Li,max} \times f(z)$ where $C_{Li,max}$ is the maximum Li concentration along the axis. Integration gives

$$C_{p,0} = \frac{C_{Li,max}}{u\tau_{diff}} \int_0^L f(z) dz. \quad (3)$$

One way to determine $f(z)$ would be from the axial variation of the Li deposition rate along the reactor wall. This, however,

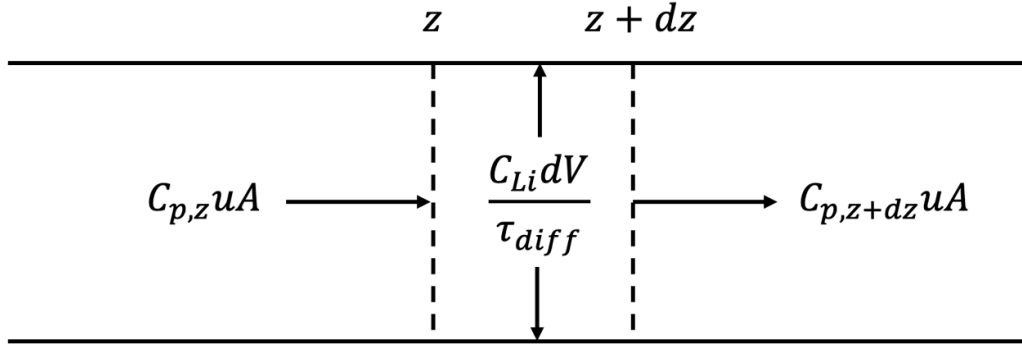


Figure 5. Schematic of the control volume used to estimate the local Li concentration using a differential mass balance.

requires time-consuming and expensive materials characterization. Instead, we used OES and estimated $f(z)$ from the easily accessible intensity of the Li 2p-2s line at 671 nm as $f(z) = I_{671}(z) / I_{671,\max}$.

The assumption that the Li concentration C_{Li} is proportional to the intensity of the Li 671 nm line is approximate because the line intensity also depends on the electron density and the excitation rate coefficient, both of which are *a priori* unknown. Hence, while the magnitude of C_{Li} is expected to be approximately correct, the axial profile of C_{Li} should be considered with caution and regarded only as an approximation. However, for the following analysis, the axial variation of the precursor concentration $C_p(z)$ is important. This variation depends on the integral of $C_{\text{Li}}(z)$, see equation (3), and thus the uncertainty in $C_{\text{Li}}(z)$ is reduced in $C_p(z)$.

For the typical conditions in table 1, $u = 3 \text{ m s}^{-1}$ and $\int_0^L f(z) dz \approx 0.054 \text{ m}$. Judish and Wunderlich measured the diffusion coefficient of Li in Ar to be $pD_{\text{Li,Ar}} = 12.3 \text{ N s}^{-1}$ [18], where p is the pressure in Pa. Hence, $D_{\text{Li,Ar}} = 0.27 \text{ m}^2 \text{ s}^{-1}$ at 340 mTorr (45.3 Pa). In [18], $D_{\text{Li,Ar}}$ was determined for a gas temperature of 563 K. Given the relatively modest plasma powers and the short residence time of the gas in the plasma ($\sim 10 \text{ ms}$), we assume that our gas temperatures may be similar. With the tube radius $R = 1.25 \text{ cm}$, we find $\tau_{\text{diff}} = 0.1 \text{ ms}$, which results in $C_{\text{Li,max}} = 2.32 \times 10^{18} \text{ m}^{-3}$. Through simple integration of equation (2) and utilizing the relationship between $C_{p,0}$ and $C_{\text{Li,max}}$ in equation (3), we can now also determine $C_p(z)$ and $C_{\text{Li}}(z)$:

$$C_p(z) = C_{p,0} \times \left(1 - \frac{\int_0^z f(z) dz}{\int_0^L f(z) dz} \right), \text{ and} \quad (4)$$

$$C_{\text{Li}}(z) = C_{\text{Li,max}} \times f(z). \quad (5)$$

Results of this simple model are presented in figure 6. The precursor concentration decreases smoothly from its initial (entrance) value of $3.2 \times 10^{20} \text{ m}^{-3}$, i.e. a mole fraction of $\sim 3\%$, to zero at the exit of the plasma zone.

The Li concentration initially increases slightly up to $z = 3.5 \text{ cm}$, which should not be over interpreted due to the rough assumptions discussed above, but then decreases rapidly because the precursor concentration decreases. The highest

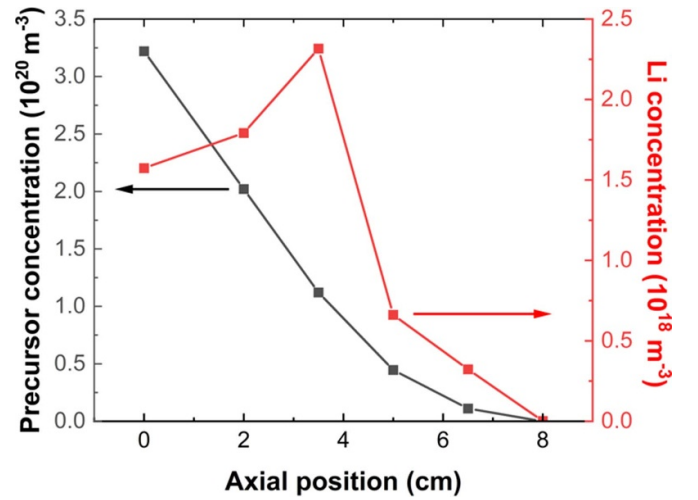


Figure 6. Axial profiles of the precursor and Li concentrations derived from the Li 671 nm emission line.

mole fraction of Li (at $z = 3.5 \text{ cm}$) from the model is only $\sim 0.021\%$. Hence Li is essentially a trace gas even though it dominates the plasma emission at the plasma entrance due to its very low excitation threshold energy and large excitation cross-section (see below). This is a direct consequence of a much faster diffusion rate in the radial direction than convection via the gas flow in the axial direction. While Si-containing precursor fragments likely have smaller diffusion coefficients than Li, leading to higher concentrations in the plasma, it seems reasonable to assume that their concentration also remains very dilute (trace).

5. Estimation of the EEDF from the Ar emission intensity ratios

Based on the discussion above, it seems reasonable to assume that the two species most affecting the EEDF are Ar and the LiHMDS precursor. Other species such as Li and Si-containing fragments likely play a smaller role because their concentrations are lower. Unfortunately, there are no known cross-sections for the LiHMDS precursor. However, one of the molecular groups in its structure is $\text{Si}(\text{CH}_3)_3$. We assume that

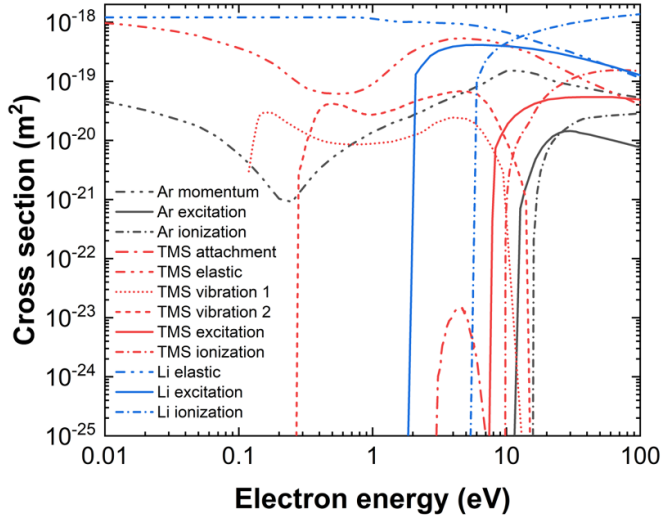


Figure 7. Elastic and inelastic cross-sections used for calculating the EEDF and the electron impact rate constants. See text for sources of the cross-section sets.

this fragment may have collision cross-sections similar to tetramethylsilane ($\text{Si}(\text{CH}_3)_4$, TMS), for which Bordage derived a collision cross-section set [19]. Hence, to at least gain qualitative insights into the effect of the precursor on the EEDF, we assume that LiHMDS cross-sections are similar to those of two TMS molecules.

The cross-section data set used in our analysis is plotted in figure 7. For Ar cross-sections, we only show the summary cross-sections from the Siglow database for clarity, which are based on [20] and the Phelps database on LXCat. However, in the Boltzmann simulations, we used the detailed cross-sections provided by the IST-Lisbon database [21], which resolves cross-sections for the excitation from the ground state for each of the individual Ar 5p and 4p levels discussed above. No cross-section set is available for the LiHMDS precursor. Therefore, we assumed that LiHMDS fragments into Li, N, and $\text{Si}(\text{CH}_3)_3$ and that $\text{Si}(\text{CH}_3)_3$ has similar cross-sections as TMS ($\text{Si}(\text{CH}_3)_4$), for which a cross-section set is known [19]. We also approximated the unknown LiHMDS cross-sections with the cross-sections of two TMS molecules. We also included Li elastic [22], Li 2s-2p excitation [23, 24], and Li ionization [25] cross-sections in the calculations to take into account the possible influence of Li on the EEDF. The inelastic 2s-2p excitation cross-section is very large and has a very low 1.85 eV excitation threshold energy.

To investigate the influence of TMS and Li on the EEDF, we calculated the electron energy probability function (EEDF) at $E/N = 50$ Td for pure Ar plasma, an Ar:TMS plasma with a molar ratio 94:6, and an Ar:TMS:Li plasma with a molar ratio of 93.98:6:0.02 (figure 8). The latter corresponds to the conditions we would expect at the position of maximum Li emission at $z = 3.5$ cm, with the precursor and Li concentration as shown in figure 6. The addition of LiHMDS has a major influence on the EEDF (figure 8) due to its large inelastic cross-sections at lower threshold energies than Ar (figure 7).

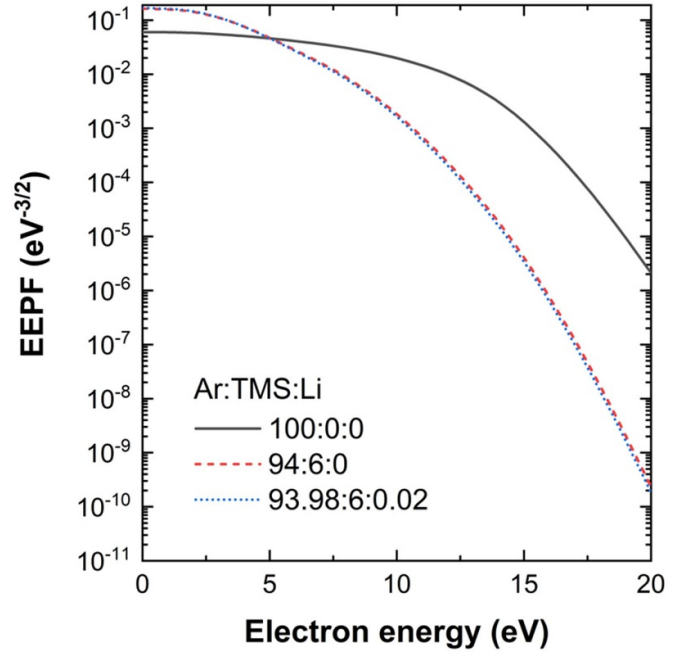


Figure 8. Comparison of the electron energy probability functions at $E/N = 50$ Td between a pure Ar discharge and Ar with 3% of LiHMDS precursor (mimicked by 6% of TMS). The effect of adding 0.021% of Li into the Ar LiHMDS mixture is also shown.

The addition of Li into the Ar:TMS mixture has an almost negligible effect, however, despite Li's large cross-sections with low thresholds, because its concentration is approximately two orders of magnitude lower than that of LiHMDS (figure 6).

We used a well-known line intensity method together with the solution of the Boltzmann equation to estimate the EEDF and the local reduced electric field (E/N) along the tube axis from the optical emission data [26–30]. First, we computed the measured Ar line ratios between each of 5p-4s lines and each of the 4p-4s lines for a total of six line ratios at each position (see figure 4(b)). To compare measured and predicted line ratios, a Corona model based on the solution of the Boltzmann equation with BOLSIG+ (version 12/2019 by Hagelaar and Pitchford [31]) was utilized to obtain relative intensities as a function of the reduced electric field. The Corona model is widely used for low-density and low-temperature plasmas [8, 32–34]. Spectral intensities of the lines can be described as

$$I_i = \frac{1}{4\pi} A_i n_{\text{ex},i} h \nu_i \quad (6)$$

where I_i , A_i , $n_{\text{ex},i}$, h and ν_i are the emission line intensities, Einstein A-coefficient for the radiative level i [17], the number density of the excited radiative species, the Planck constant, and the emission frequency, respectively. The rate balance equation for an excited state i of Ar is given by

$$n_{\text{ArI}} n_e X_{\text{ex},i} \left(\frac{E}{N} \right) = n_{\text{ex},i} \left(\sum_j A_j \right)_i \quad (7)$$

where n_{ArI}, n_e and $X_{\text{ex},i} \left(\frac{E}{N} \right)$ are the number density of the Ar I ground state, the electron density, and the rate coefficient of Ar I excitation as a function of the reduced electric field, respectively. The rate coefficient of the excitation is

$$X_{\text{ex},i} = \int_0^\infty v \sigma(\varepsilon_e) f(\varepsilon_e) \sqrt{\varepsilon_e} d\varepsilon_e \quad (8)$$

where $\sigma(\varepsilon_e)$ and ε_e are the excitation cross-section from the ground state and the electron energy ε_e , v is the electron speed and $f(\varepsilon_e)$ is the EEPF, determined by BOLSIG+: EEPF is related to the EEDF by multiplying with $\sqrt{\varepsilon_e}$.

From equations (6) and (7), line emission intensities are

$$I_i = \frac{A_i}{4\pi \left(\sum_j A_j \right)_i} n_{\text{ArI}} n_e X_{\text{ex},i} \left(\frac{E}{N} \right) h\nu_i. \quad (9)$$

Thus, the predicted line intensity ratio for two lines i and k can be described as

$$R_{ik} = \frac{I_i}{I_k} = \frac{\frac{A_i}{\left(\sum_j A_j \right)_i} X_{\text{ex},i} \left(\frac{E}{N} \right) \nu_i}{\frac{A_k}{\left(\sum_j A_j \right)_k} X_{\text{ex},k} \left(\frac{E}{N} \right) \nu_k}. \quad (10)$$

BOLSIG+ was utilized to calculate the excitation reaction rate coefficients $X_{\text{ex},i} \left(\frac{E}{N} \right)$ with cross-section data discussed above and the line intensity ratios are expressed as a function of the reduced electric field.

We examined all six line ratios for accuracy by testing whether E/N values required to reproduce the experimental line ratios were physically reasonable. Line ratios can deviate from the simple Corona model used here for various reasons, including cascade excitation of the upper level or significant excitation from metastable and resonant states. We found that of the six ratios of the lines listed in table 2, only the ratios using the 750.4 nm and 751.5 nm lines yielded E/N values that were consistent with a simple ionization balance: i.e. a balance that requires that the total ionization frequency predicted by BOLSIG+ is the same as the ambipolar diffusion loss frequency. Hence only these four line ratios were used in the analysis. The other two line ratios yield reduced electric fields, E/N , that were significantly smaller.

The reduced electric field was found by minimizing an error function

$$\mathcal{E} \left(\frac{E}{N} \right) = \sum_{i,k} \frac{(R_{ik,m} - R_{ik,t})^2}{(R_{ik,m} + R_{ik,t})^2} \quad (11)$$

where the sum is over the squared values of the difference between the measured and calculated values of the four line ratios based on the blue 415.9 nm and 420 nm lines and the red 750.4 nm and 751.5 nm lines.

Results of this analysis using the line ratios are shown in figure 9. E/N varies between 25 and 35 Td upstream and between the electrodes. It increases sharply to 60 Td downstream of the electrode, where the validity of our model

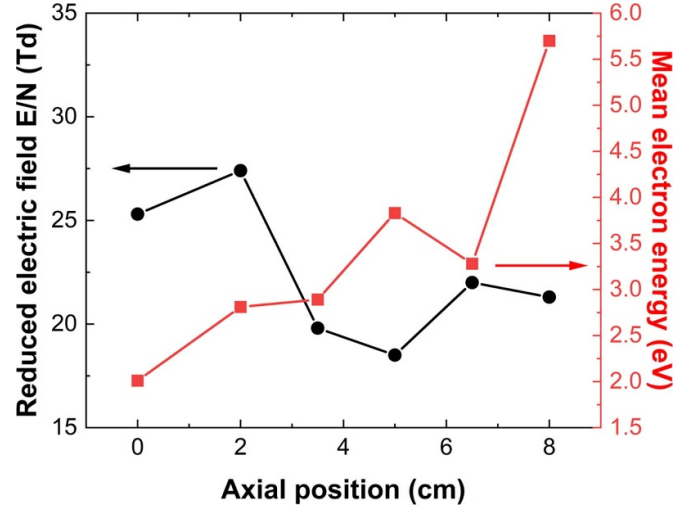


Figure 9. Predicted reduced electric fields and mean electron energies along the discharge axis using the line-ratio method described in the text.

degrades because the Corona model is unlikely to be valid in the plasma afterglow region, where the effect of convected metastable atoms may be appreciable. Despite the relatively constant E/N between the electrodes, the mean electron energy increases essentially continuously. This increase is attributed to the continued consumption of the LiHMDS precursor along the axis, decreasing its concentration. As the precursor with large cross-sections (figure 8) and threshold energies significantly lower than those of Ar decreases, the mean energy rises, as shown in figure 9.

Figure 10 shows the EEDFs based on our analysis. The mean electron energy increases with increasing axial position due to continued precursor depletion along the axis. This leads to ‘flatter’ EEDFs (referring to higher apparent electron temperature) in the low energy range of the EEDF. We suggest that this is essentially the reason for the changing Li-to-Si ratio of the films along the discharge axis. The Li–N bond energy is 2.2 eV [35], so the dissociation of this bond should have an onset at this threshold energy. The cross-section for electron attachment to TMS has threshold energy of 3 eV and a peak at 4 eV. Some of these electron attachment events will lead to dissociation (i.e. dissociative attachment). Hence, an increase in electron temperature may lead to enhanced dissociation of the TMS-like $\text{Si}(\text{CH}_3)_3$ groups relative to dissociation of the lower threshold Li–N bond. This may explain the reduction of the Li-to-Si ratio observed in our experiments, reflecting the enhanced dissociation of $\text{Si}(\text{CH}_3)_3$ with decreasing precursor concentration. At the same time, the axial depletion of the precursor also causes the reduced film deposition rate shown in figure 2.

We acknowledge that the full electron-impact driven dissociation kinetics of LiHMDS in plasmas is much more complicated than is captured by the simple analysis presented here. Moreover, the surface conditions may also influence the fragmentation mechanisms of LiHMDS, as shown in recent studies of atomic layer deposition using LiHMDS [36, 37]. However, in the absence of electron-collision cross-sections

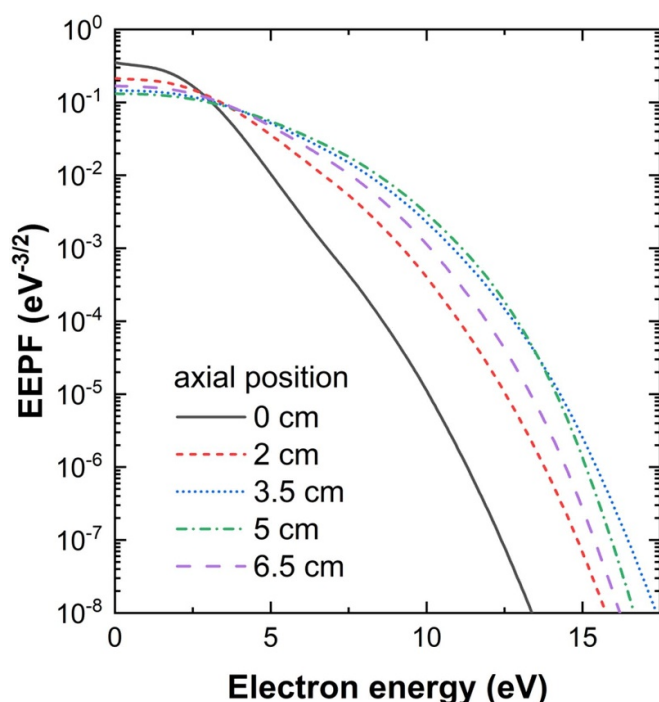


Figure 10. Electron energy distribution functions at different axial positions based on the spatial variation of the reduced electric field E/N shown in figure 9 and the gas composition shown in figure 6.

for LiHMDS and of surface sticking coefficients for its fragments, a more accurate modeling is currently not possible.

6. Conclusions

We demonstrated the synthesis of Li_xSi_y films by PECVD from LiHMDS diluted in Ar plasmas and developed a simple one-dimensional (1D) transport model for the deposition process. The Li-to-Si ratio in the films varied as a function of axial position from 3:1 (Li:Si) at the beginning of the plasma to 1:1 downstream of the plasma. The simple 1D transport model captured this experimentally measured trend and suggested that it is related to the decreasing precursor concentration along the axis. Specifically, the model suggests that decreasing precursor concentration along the axis increases the mean electron energy (electron temperature). This increase in mean energy favors the enhanced dissociation of $\text{Si}(\text{CH}_3)_3$ groups, with a threshold of 3 eV, compared to Li–N bonds, with a lower threshold of 2.2 eV. This may explain the axial decrease of the Li-to-Si ratio in thin Li_xSi_y films.

Overall, this study demonstrates the challenges of controlling the atomic composition in thin films of species with strongly differing dissociation energies. The mechanisms discussed here could be utilized in a variety of ways. For instance, axial flow systems such as the one discussed here combined with axially moving substrates could be designed for the deliberate deposition of films with graded chemical composition. Chemically uniform films could be achieved in stagnation flow reactors using a shower head design for precursor delivery.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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