Charge-state-resolved ion energy distributions of aluminum vacuum arcs

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The charge-state-resolved ion energy distributions of metal ions present in a cathodic arc plasma have been measured and analyzed. Contrary to literature data, lower energies were observed for higher charged ions. The observations were explained by opposing acceleration by pressure gradient and electron-ion coupling, and deceleration by part of the discharge voltage. The distributions were well fitted by shifted Maxwellian distributions, giving additional information on plasma parameters. These results are of importance for an improved understanding of the evolution of ion energy distributions, and is hence instrumental for future progress in thin film growth modelling.

Vacuum arc plasma is well known to be highly ionised with high directed energies (averages for most materials between 20 and 150 eV),[1] which is of importance for synthesis of dense coatings with the ability to control their structure evolution. Most energy studies deal with the average or the most likely energy in the plasma, or they describe ion energy *distributions* (IEDs) including all ion species present.[2-6] The experimental data available on the dependence of the IED on ion charge state are rather contradictory.[7-13] Davis *et al.*[8] and Miller[9] showed an increasing ion energy with increasing charge, while Bugaev *et al.*,[10,11] Yushkov *et al.*,[12] and Chhowalla[13] reported that energy distributions are approximately independent of ion charge state.

Several theories have been suggested to account for ion acceleration mechanisms with resulting energies. The two most referred to are the potential hump theory[2] and the gasdynamic model[14]. The former predict ion formation near a peak of the discharge voltage profile and acceleration due to the electric field, and the latter states that electron-ion friction and expansion cooling (pressure gradient) are the main mechanisms responsible. Adjustments to these models[15,16] and further investigations[12,17] have been made but there is still a lack of reliable, charge-state-resolved IEDs data, which can confirm or suggest the main acceleration mechanisms.

In this Letter, we present examples of detailed measurements and analysis of charge-state-resolved IEDs of metal ions present in aluminum vacuum arc plasma. The experimental distributions are fitted with shifted Maxwellian distributions, where the fitting parameters may provide information on the plasma properties. The investigation is of importance to an improved understanding of ion acceleration mechanisms and resulting IEDs, and hence for future advancement in thin film growth modelling.

Vacuum arc plasma was generated from a conical aluminum cathode (base and top diameters 51 and 12 mm, respectively, and height 38 mm), powered by a direct current (dc) arc supply, with resulting arc current of 35 A. The arc was triggered by a voltage flashover across a ceramic tube between a trigger electrode and the cathode. The cathode spots were confined to the cathode surface by a permanent ring magnet located behind the cathode. All measurements were performed in oil-free vacuum at a base pressure of about 1×10^{-4} Pa, and at a distance of 45 cm from the cathode. Initial plasma characterisation was carried out using a Langmuir probe in the form of a 10.25 mm long Pt wire exposed to the plasma (Fig. 1). The plasma potential was found to be positive, approximately 3 V with respect to the anode (ground). Furthermore, a mass-energy-analyser (PPM-422, Pfeiffer Vacuum) was used to determine plasma chemistry through a mass-to-charge measurement at fixed energy, and IEDs through energy measurements at fixed mass-to-charge ratio. The entrance orifice of the mass-energy-analyser was grounded. The Langmuir probe was retracted for IED measurements.

A mass-to-charge measurement at 50 eV, showed Al^{1+}, Al^{2+}, and Al^{3+} as the most abundant ions, as well as small traces (in total less than 1%) of hydrogen, oxygen and nitrogen ions. Consequently, measurements of IEDs were limited to the three metal ions, see Fig. 2. In order to represent a smoothened IED with no high frequency fluctuations in the distribution, Fourier components with frequencies higher than $\Delta t/n$ where removed, where n is the number of data points considered at a time, and Δt is the spacing between two adjacent data points. In the IED, every 1-eV step is divided in 16 data points, and smoothening was done over a range of 5 eV. The resulting IEDs are shown in Fig. 3, where one can clearly see differences between the different ions: In contrast to previous reports in the literature, higher charged ions show lower energies; measured averages corresponding to 53.8, 44.2 and 42.9 eV for Al^{1+}, Al^{2+} and Al^{3+}, respectively. The reproducibility of this fundamental result was shown in four repeated series of measurements. Each time the same trend was observed. The difference in measured average energy (i.e. no correction due to the difference of plasma potential and orifice potential) between Al^{1+} and Al^{2+} was in the range 9.6-12.9 eV, and the difference Al^{2+} and Al^{3+} was 1.2-3.6 eV. Neither the potential hump theory nor the gasdynamic theory can explain the here-observed charge-dependent differences of the IEDs, namely that *lower* average energies exist for *higher* charged ions: The average energies are neither proportional to the charge state (potential hump) nor approximately equal (gasdynamic model). Furthermore, higher charged ions should be more accelerated if electron-ion coupling (Q^2 dependence) dominated ion expansion and acceleration.[15]

A possible explanation can be found considering the electric field due to the discharge´s voltage drop. In a vacuum arc, ions are accelerated *against* this field, and thus in the “wrong” direction. Therefore, as the ion is formed, it may be decelerated over a potential drop U (part of the discharge voltage). The differently charged ions are formed at different distances from the cathode surface through successive freezing of the ion charge state ratios, as described in the model of partial local Saha equilibrium (PLSE).[18] Based on this model U can be estimated assuming that the ion is accelerated by (i) ion pressure gradient (P) (ii) electron-ion coupling with the much faster drifting electrons (C), and (iii) electric field corresponding to U. The results of the approximation show that $P > |U| > C$, with a lower limit of $|U|$ around 13 V, hence about half of the here-measured discharge voltage of 26 V.

To gain additional information on the plasma parameters, the distributions were fitted by shifted Maxwellian distributions (SMD), as proposed by Kutzner *et al.*[7] Bilek *et al.*[19] adopted this approach to describe IEDs of Ti^{+} ions in a nitrogen environment. The forward ion flux distribution of a SMD can be written as

$$f(E) = C_s\left[E - QV_p\right] \cdot \exp\left[-\left(\sqrt{E - QV_p} - \sqrt{V_{dir}}\right)^2 / T\right] \tag{1}$$

where C_s is a scaling constant, V_p is the plasma potential with respect to the reference voltage of the analyser (0 V = ground), V_{dir} is the directed energy (center-of-mass energy) of the ions, Q the charge state, and T is the temperature (or random energy). The terms containing Q are introduced to correct for the increase in ion energy due to the difference between plasma potential and analyser entrance (ground). C_s, V_{dir}, and T were varied as to obtain the best fits (minimised error function) to measured IEDs.

Fig. 3 shows that the IEDs can be well described by shifted Maxwellian distributions, with fitting parameters as presented in Table I. Since only the forward flux of the ions is measured, the fitting parameters indicate if the high average energies are due to a high directed energy (V_{dir}) of the distribution, or a very broad distribution (high T). For approximately the same temperature (width of the distribution), a lower average energy corresponds to a lower directed energy. This is observed for Al^{1+} and Al^{2+}. For the parameters of Al^{3+}, the large difference between average energy and directed energy is explained by the high temperature (broad distribution).

The discrepancy directed energy as well as temperature between Al^{3+} on one hand and Al^{1+} and Al^{2+} on the other hand, can be explained by charge exchange collisions. Recent findings[20] have shown that neutrals are present in cathodic arc plasmas; the sources are not only evaporating macroparticles and hot craters but self-sputtering that occurs when energetic ions condense on substrates and walls. These neutrals will cause some of the highly charged ions to cascade down to lower charge states. Since the plasma is dominated by Al^{1+} and Al^{2+}, the charge exchange collisions will be most observable from a change in the IED of Al^{3+}. It has previously been reported[19] that interaction (including charge transfer) between expanding plasma and gas molecules resulted in decreasing peak energies of the IEDs with increasing pressure, but with accompanying difficulties to eliminate energetic ions in the high energy tail. Correspondingly, charge transfer reactions between neutrals and Al^{3+} will mainly result in a decreased maximum intensity of the Al^{3+} IED, while the high energy tail is maintained. The shifted Maxwellian distribution will become broader, which is equivalent to a higher temperature.

If we assumed that the highly charged ions had higher energies than the lower charge states before charge exchange occurred, charge exchange would increase the average energy of lower charges but never beyond the energy of the higher charge states. Given the here presented experimental data, this assumption is not supported. In the opposite case, assuming higher charged ions have lower energy than the lower charged before charge exchange collisions, e.g. due to the decelerating field, charge exchange would decelerate lower charge states but not below the energy of the higher charge state. This is consistent with the measured data, however it may be difficult to quantify due to the competing accelerating and decelerating forces.

The measured discharge voltage is somewhat higher than previously reported values in literature,[1] which may be due to the magnetic field at the cathode surface from the ring magnet. However, this field should not greatly affect the results, since it is the *gradient* of the field that can lead to ion acceleration and deceleration.

Yet another factor affecting the interpretation is the inherently large-scale fluctuations of all plasma parameters caused by non stationary cathode processes.[21] It is important to keep in mind that the observed distribution functions are averages, and that instantaneous distributions may vary largely.

We here measured that the IEDs show lower energies for higher charged ions, and can be well described by shifted Maxwellian distributions with related fitting parameters. The here presented ion energy data can be understood by considering the effect of opposing forces active near the cathode spots: In summary, *acceleration* by pressure gradient (which includes the electron pressure gradient) and electron-ion coupling, and *deceleration* by part of the discharge voltage. These results are of importance for an improved understanding of the evolution of ion energy distributions, and is hence instrumental for future progress in thin film growth modelling.

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Figure caption:

Figure 1: Schematic of the experimental setup.

Figure 2: Measured ion energy distributions (raw data).

Figure 3: Smoothened (not shifted) ion energy distributions (of raw data in Fig. 2) with fitted shifted Maxwellian distributions (SMD).

Fig 1, Rosén et al, APL

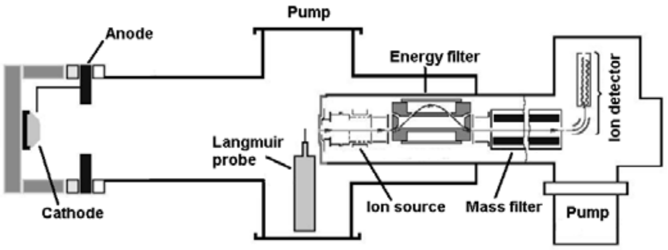

Fig 2, Rosén et al, APL

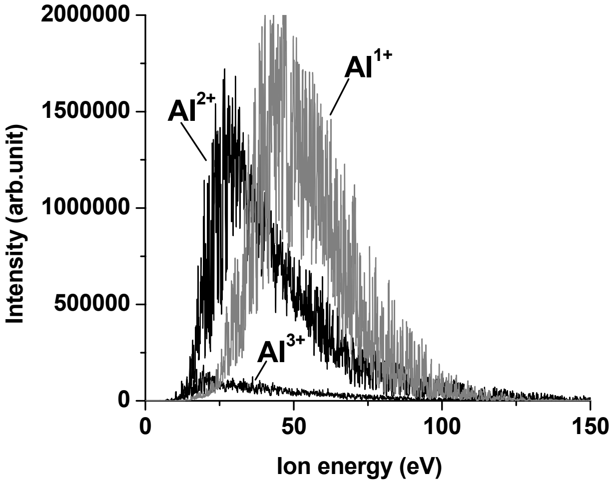

Fig 3, Rosén et al, APL

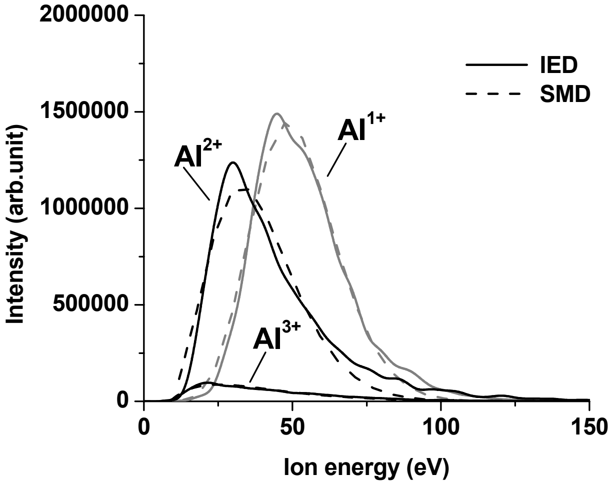

Table I, Rosén et al, APL

Table I: Average energy (E_{ave}) and fitting parameters (directed energy V_{dir}, temperature T, scaling constant C_s) used in Eq. (1) to fit the measured IEDs.

	Al^{1+}	Al^{2+}	Al^{3+}
E_{ave} (eV)	53.8	44.2	42.9
V_{dir} (eV)	40.9	18.9	0.5
T (eV)	2.3	4.3	16.2
C_s	33522	49143	14396