Plasma electrochemical growth of ion-conducting AgBr and AgCl

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Abstract

The electrochemically controlled anodic growth of binary cation-conducting layers in reactive low temperature plasmas is studied (model systems: AgCl and AgBr). A formal stability criterion comparing the electric field within the film and the plasma is derived. It predicts either morphologically stable or unstable growth depending on the reaction temperature. The experiments prove this stability criterion qualitatively. The experimental setup and results of our plasma electrochemical growth experiments are presented. The idea to utilize low temperature plasmas as 'fluid mixed conductors' is discussed.

1. Introduction

The idea to apply plasmas as 'gaseous electrolytes' is relatively old. First experiments with a cell of the type Me|air plasma|aqueous AgNO$_3$-solution were already performed in the 19th century [1]. A reaction was performed directly at the surface of the ion-conducting liquid electrolyte, leading either to the deposition of a thin silver film or the release of oxygen. These first plasma electrochemical experiments have been long forgotten since, mainly due to the missing applications in the fields of liquid electrolytes.

Within the last two decades, the need for thin films led to an enormous interest in plasma-assisted techniques, and thus, also a number of ion-conducting solid films have been prepared in experiments comparable to the approach by Gubkin [2–7]. However, in the vast majority of plasma-assisted techniques—like PECVD or sputter-coating processes— a more or less inert substrate is covered by a thin film originating from precursors in the gas phase. An electric substrate bias is generally not applied.

In the present study, cation conducting films are produced by a different plasma electrochemical approach, which is depicted schematically in Fig. 1. The solid electrolyte AX$_\nu$ supplies cations A$^+$. These cations are transported through the electrolyte from the anode metal A to the interface with the ionized electronegative gas. The plasma supplies free electrons, cations, anions and the electronegative neutral component. At the plasma/electrolyte interface, the product is virtually formed from cations supplied by the solid electrolyte and from anions (or neutral species and electrons) supplied by the gaseous electrolyte. Thus, the solid electrolyte is directly in-

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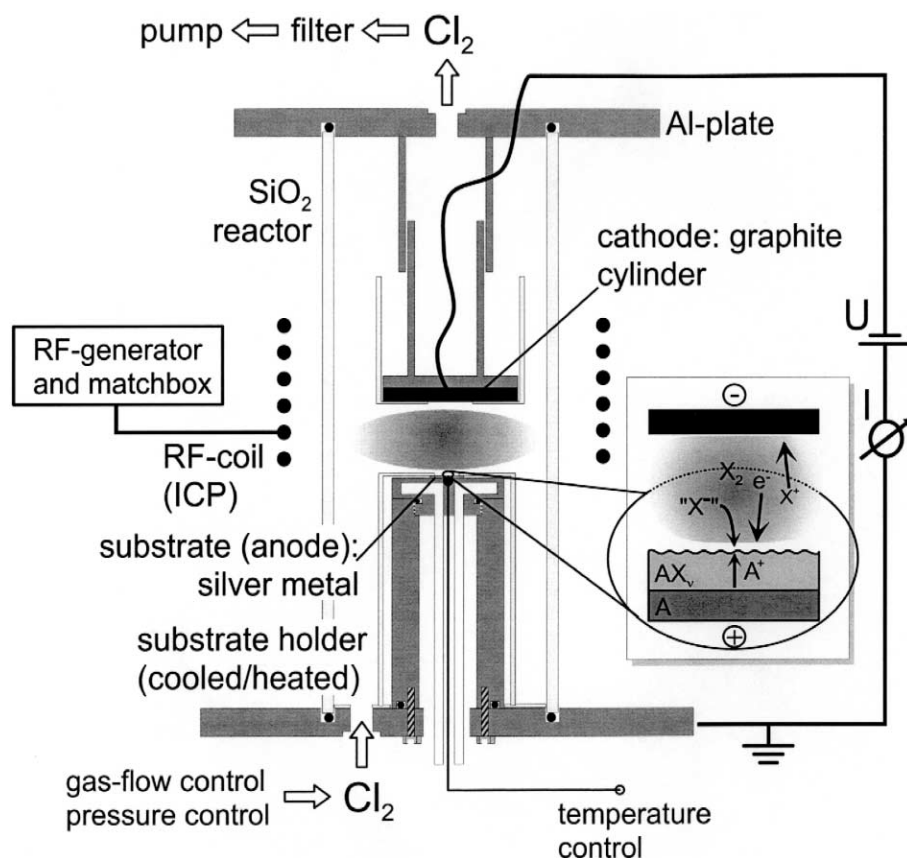*E-mail address:* janek@phys.chemie.uni-giessen.de (J. Janek).

Fig. 1. RF-plasma reactor (ICP) for the oxidation of metals in reactive plasma. Inset: schematic representation of the plasma anodization (anodic DC-bias) and the growth of a solid electrolyte in an inductively coupled plasma.

volved in the growth process as an electrochemically active substrate. In a simple experiment, the metal A is used as a starting material, forming the electrolyte AX_ν in situ. In other words, a plasma anodic oxidation of metal A is performed.

It is expected that the application of an external electric field leads to a different kinetics of an oxidation process if an ionic compound is formed [8]. The electronic and the ionic fluxes within the growing compound film are decoupled by the flux of electrons via the plasma, the Nernst–Planck coupling that controls the parabolic thermal growth is replaced by a more complicated dependence of the growth rate on the electric current and on the chemical driving force. For a systematic study of the kinetics and the morphology of the growing cation-conducting films, we chose the well-studied silver halides

[9–11] as model systems. The results of this experimental study are summarized in the following.

2. Morphology of 'plasma electrochemically' grown films

The morphological stability of moving phase boundaries has been discussed extensively by Schmalzried [12] and is exemplified by a number of different experiments by Martin and Schmalzried [13]. In any case, the local driving force (electric, chemical or temperature field) has to be analyzed as a function of the externally applied force in order to discuss the morphological development. In the present case, we regard the plasma as a mixed-conduct-

ing fluid, in which electronic conduction prevails. The solid electrolyte is cation-conducting with thermally activated charge carriers. In accordance with Schmalzried, we simplify the stability criterion to the following result, assuming homogeneous phases: If the rate limiting flux points in the same direction as the movement of the phase boundary, the phase boundary should be morphologically stable. This would be the case if the cation flux were rate-determining. If the flux of electrons in the plasma rules the kinetics of the growth process, the growing product should try to short-circuit the plasma and the growth becomes unstable (Fig. 2).

Our idea is to control the morphological development of the product surface simply by the reaction temperature. Since the plasma conductivity is much less temperature-dependent than the conductivity of the solid electrolyte, we should be able to change from the condition $\sigma(\text{plasma}) > \sigma(\text{electrolyte})$ to $\sigma(\text{plasma}) < \sigma(\text{electrolyte})$. At low temperatures, the phase boundary should grow stable and at higher temperatures, it should become unstable during growth. Of course, the morphology itself cannot be predicted by a stability analysis.

This simple stability criterion represents only a first-order approximation and should not be overem-

phasized. Whereas the assumption of a homogeneous solid electrolyte phase is surely valid, the local conductivity in a plasma is not constant, rather it is strongly dependent on the local field and the plasma conditions. Furthermore, sputtering effects by ion bombardment have not been taken into account as a side effect.

3. Experiments

3.1. Experimental setup

The self-constructed vacuum chamber for the experiments is shown in Fig. 1. It consists of a silica glass tube (outer diameter 100 mm; length 250 mm), which is flange mounted by O-rings to aluminum plates. The substrate holder can be either heated or cooled and is grounded in the electrochemical experiment. The second electrode on top consists of a massive graphite cylinder. The bias is applied to the graphite electrode relative to ground and can be varied between ± 210 V (Keithley Sourcemeter 2400). The substrate can be heated up to 200°C using a heating liquid. The RF generator (Hüttinger PFG 300 RF) is coupled inductively to the plasma. An automated system (MKS 647B mass flow and pres-
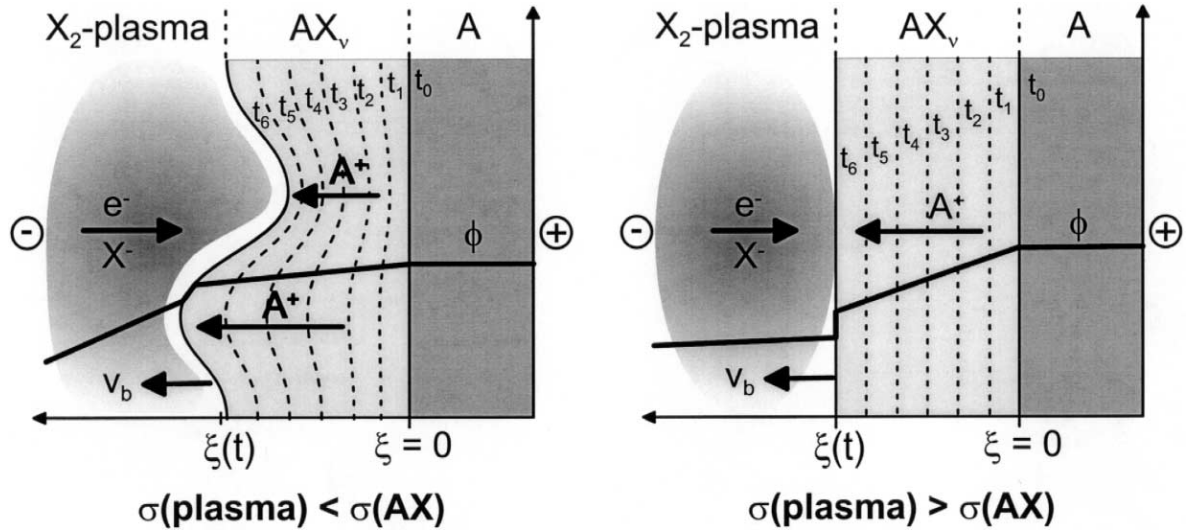

Fig. 2. Limiting cases for the morphological development of a solid electrolyte film (surface velocity v_b) growing by plasma-anodic metal oxidation: The flux of the cations in AX_v follows the electrical field. If the conductivity of the solid electrolyte is higher (lower) than the conductivity of the plasma, the solid phase grows morphologically unstable (stable). t denotes different reaction times, and ϕ denotes the galvanic potential.

sure programmer) is used to control the gas flow and the gas composition as well as the pressure. The temperature is measured with an electrically insulated thermocouple equipped with a protecting metal sheath, which is plugged via a ferrite coil to a Voltmeter (Keithley DMM 2001). The whole setup is controlled by a PC.

The RF power coupled to the plasma controls the ion density in the plasma and the geometrical extension of the plasma. The DC-Bias is used to control the current across the electrolyte/plasma interface. The gas composition primarily determines the chem-

ical potential of the reactive component—a continuous gas flux of about 5 sccm was maintained in order to keep the gas composition constant.

3.2. Oxidation experiments

Polished silver plates with a diameter of 15 mm were used as substrates. After the experiments, a white product layer covered the substrates. The morphology of the product layer showed a good lateral uniformity. EDX- and X-ray diffraction give clear
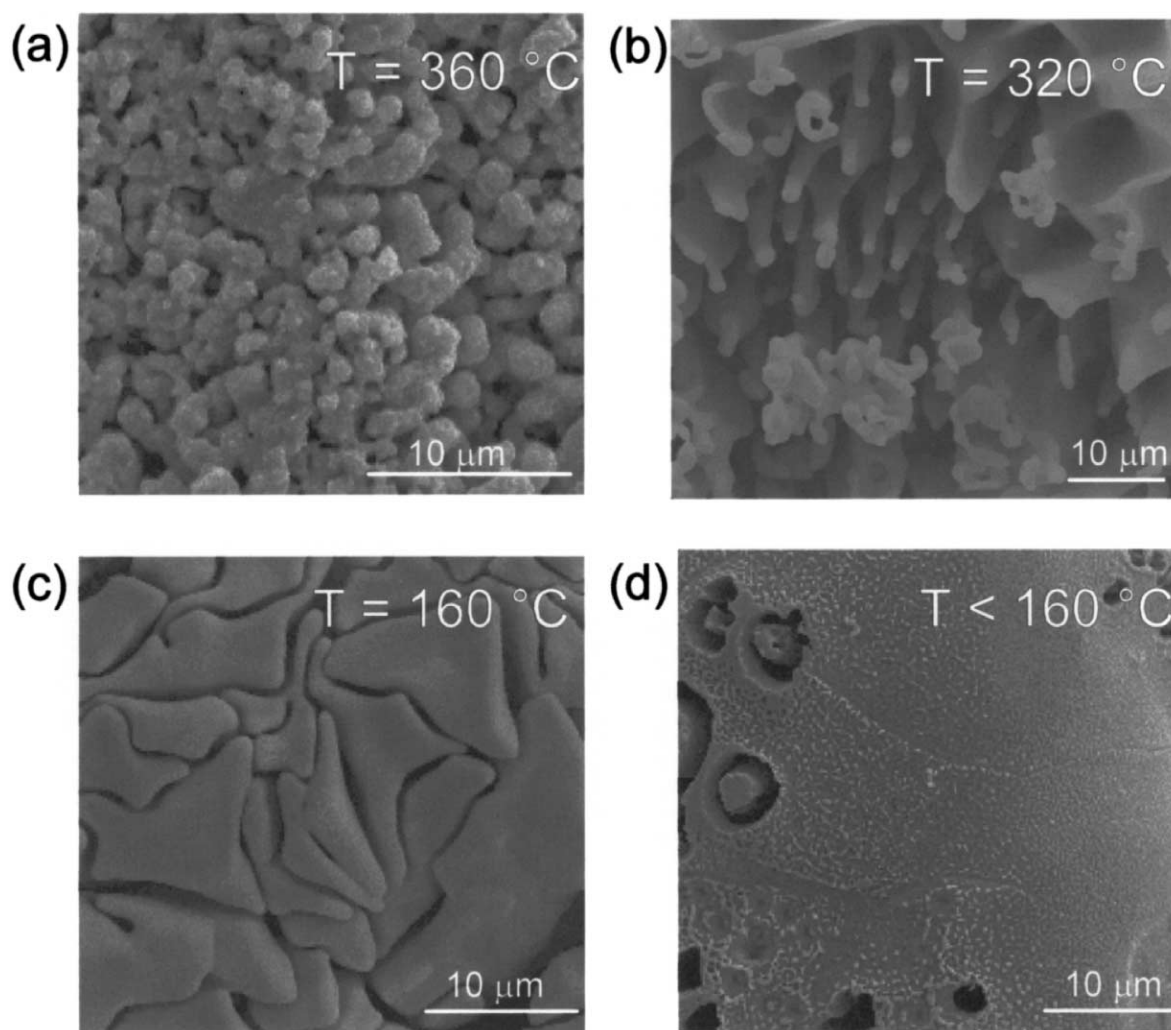

Fig. 3. SEM micrographs of AgBr product layers grown in a μW-bromine plasma at different substrate temperatures (a–d). The surface morphology of the grown films depends on the substrate temperature.

evidence for polycrystalline silver chloride as the only product.

4. Results and discussion

First plasma electrochemical experiments in our laboratory have been performed in a DC-bromine plasma [14]. Silver bromide was grown on single crystalline silver chloride substrates. The new phase grew dendrite-like but also other fragile morphologies were found. DC-plasma experiments are cheap and require only minor equipment but suffer from a serious disadvantage in respect to plasma electrochemical reactions. The substrate potential cannot be controlled without influencing the plasma itself directly.

Consequently, the growth of AgBr via the oxidation of silver was studied in a bromine microwave (μW) plasma. As outlined above, the influence of the substrate temperature on the product morphology was examined primarily.

A main result is shown in the scanning electron micrographs of the product layers in Fig. 3. The product morphology is dependent on the substrate temperature, Fig. 3a shows a layer grown at 360°C. The product consists of grains with a fractal appearing substructure. The average size of the grains equals a few micrometers. An oxidation performed at 320°C shows a finger-like morphology, and the typical size of the structures is about three times larger than those in the first picture (see Fig. 3b). Further decreasing the temperature, the morphology development becomes almost stable (160°C, cf. Fig. 3c). The average length of the disturbances equals now more than 10 μm. Below 160°C, an almost flat and stable morphology is obtained (Fig. 3d).
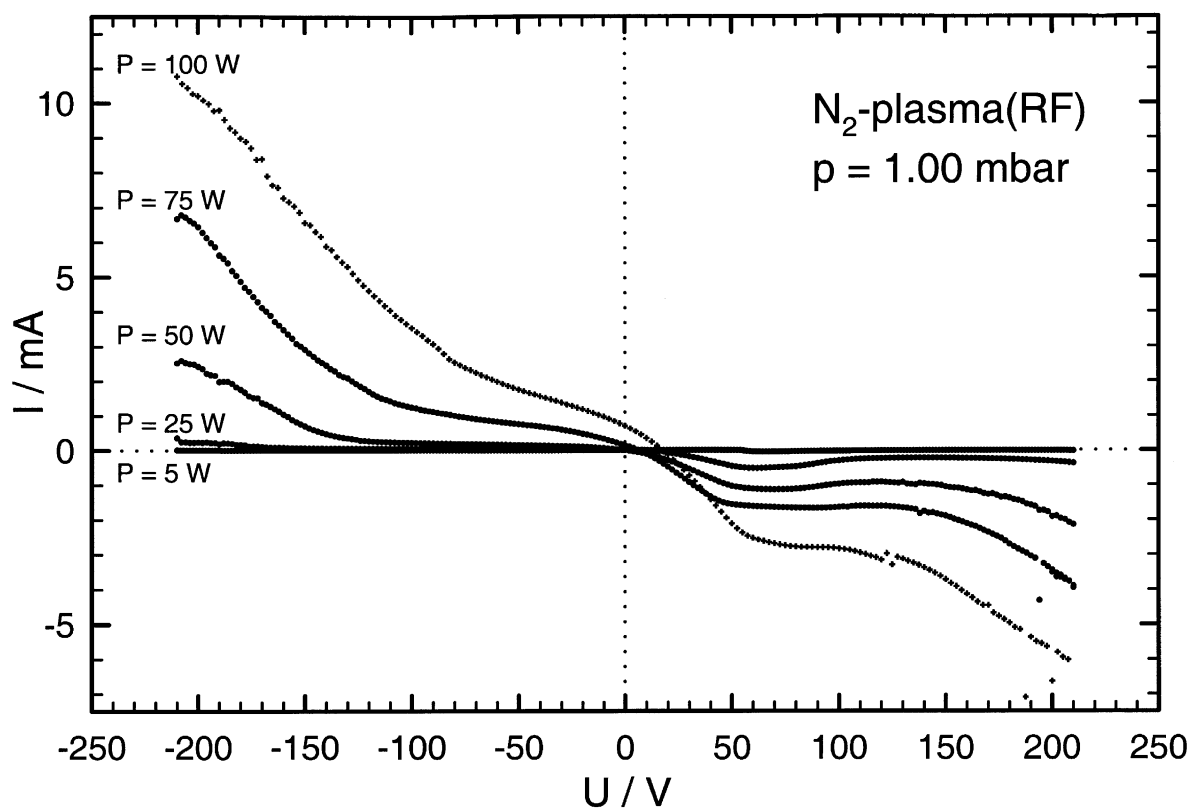

Fig. 4. The voltage–current characteristics of a nitrogen RF-plasma at varying (5–100 W) RF power (electrode distance: 3.5 cm; anode diameter: 1.0 cm; room temperature).

In the present study, a radio-frequency (RF) plasma is applied. It has typically a lower power density than a μW-plasma but a better homogeneity due to the long wavelength of the RF radiation. The inductively coupled plasma (ICP) as applied here is an electrodeless plasma, and thus, fulfills our requirements for plasma electrochemical reactions.

4.1. Plasma characterization

Whereas the plasma bulk is quasi-neutral, there are always distinctive space charge regions at the walls of a reactor and at electrodes. If an external voltage is applied, most of the voltage drop occurs in the space charge regions at the electrodes.

A consequence of this well-known behavior is a strongly non-linear voltage–current characteristics of two electrodes immersed in a plasma (Figs. 4 and 5),

cf. the behavior of Langmuir probes [15]. Due to the different sizes of our electrodes, a 'self-bias' is established. Symmetric voltage–current characteristics resulted after modifications of the reactor geometry, i.e. primarily of the electrode areas.

The conductivity of a plasma also depends on the chemical nature of the gas, which determines its ionization properties. A chlorine gas shows a lower conductivity than a N_2 plasma at equal RF power, caused by a lower degree of ionization. Furthermore, the electronegative gas traps electrons and forms negative ions. This reduces the electron density and correspondingly the conductivity.

4.2. The growth kinetics

The growth rate was measured at constant RF power and different DC-bias within the range ± 210
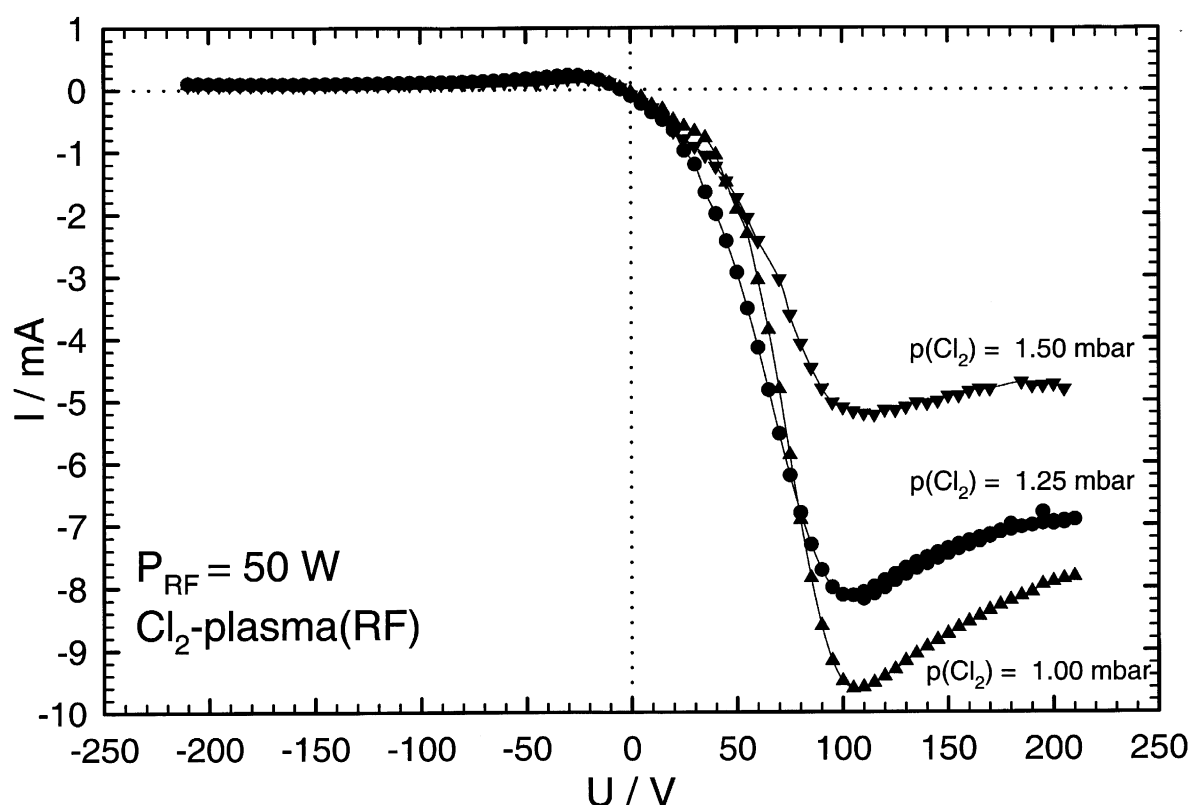

Fig. 5. The voltage–current characteristics of a Cl_2 RF-plasma at different gas pressures (electrode distance: 3.5 cm; anode diameter: 10 cm; room temperature).

V. After each experiment, the mass change of the substrate was measured, and the mean thickness of the product layer was calculated on the basis of simple geometric assumptions (Fig. 6). After 1 h of reaction time, a film thickness up to 40 μm was found, whereas in a standard thermal oxidation an AgCl layer thickness of much less than 1 μm is typically found. The voltage dependence is straightforward: at anodic potentials, the oxidation rate increases linearly with the applied voltage. Applying cathodic potentials, one expects the impact of positive ions on the surface. This could lead to a sputtering of the surface and a corresponding decrease of the weight of the substrates. However, no significant weight loss occurred within 1 h. The diagram (Fig. 6) can also be interpreted on the basis of the voltage–current characteristics in Fig. 5. The observed oxidation rate is a direct consequence of the anodic current.

In Fig. 7, the electric charge flown during the growth experiment is plotted versus the mass change of the different samples. A linear relation is obtained, but the electrochemical yield of the reaction equals only half of the expected yield corresponding to Faraday's law. Two explanations for this discrepancy are possible: either half of the produced film is simultaneously removed by anion sputtering, or leakage currents due to imperfect insulation of the Aluminum sample holder is responsible.

4.3. Surface morphology of the product layer

The surface morphology of silver chloride films grown at different temperatures in a RF plasma are shown in Fig. 8 by SEM pictures with two different magnifications. The films grown at 50°C show an almost planar and regular surface. Silver chloride hillocks can be seen on the surface. At 100°C, a
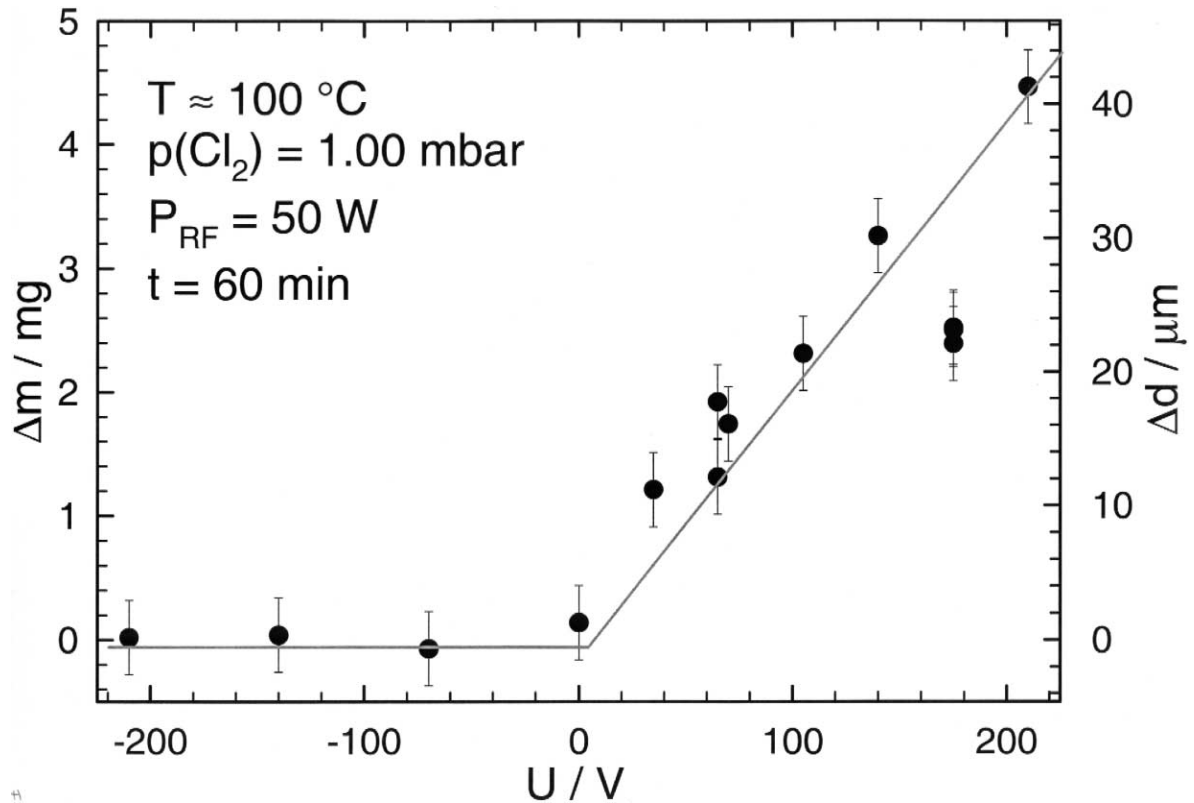

Fig. 6. Mass increase of silver substrates due to the growth of AgCl in a pure chlorine RF-plasma at different DC-bias after 1 h of reaction time.
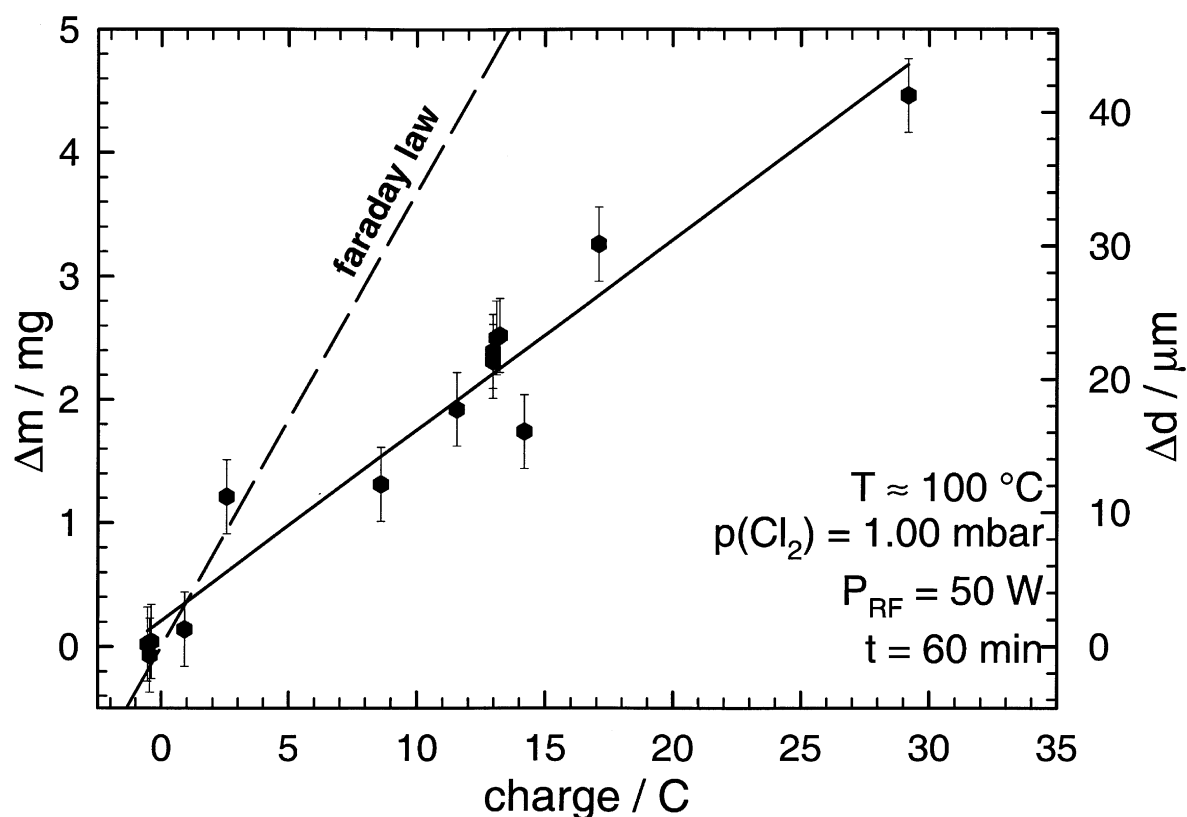
Fig. 7. Mass increase of silver substrates in a chlorine RF-plasma versus the flown charge, cf. Fig. 8.

completely different morphology appears. The silver chloride crystals grow in a needle-like form. In the right picture, which was taken under an angle of 45°C, it can be seen that the growth of these needles occurs in domains. At higher temperatures, the morphology of the films becomes even more fragile, showing fan-like structures.

Of major importance for the plasma properties is the geometry of the plasma chamber. Small changes of the reactor geometry influence the plasma and the local electric potential severely. Thus, also the surface morphology of the product layer is extremely sensitive to the reactor geometry. The appearance and properties of the plasma depends not only on the well controllable boundary conditions, but also on the treatment of the reactor walls and the exact geometry of the experimental setup. The surface morphology changes on slight variations of these

parameters and an exact reproduction of specific morphologies is not yet possible.

5. Conclusions

The plasma electrochemical growth of cation-conducting AgCl on Ag has been performed under well-defined thermodynamic conditions in a chlorine RF plasma. We have proven that the growth kinetics can be controlled with electrochemical methods. A linear dependence of the growth rate on the electric current across the plasma electrochemical cell Ag|AgCl|Cl$_2$-plasma|C is found. However, significant anodic sputter effect seem to occur.

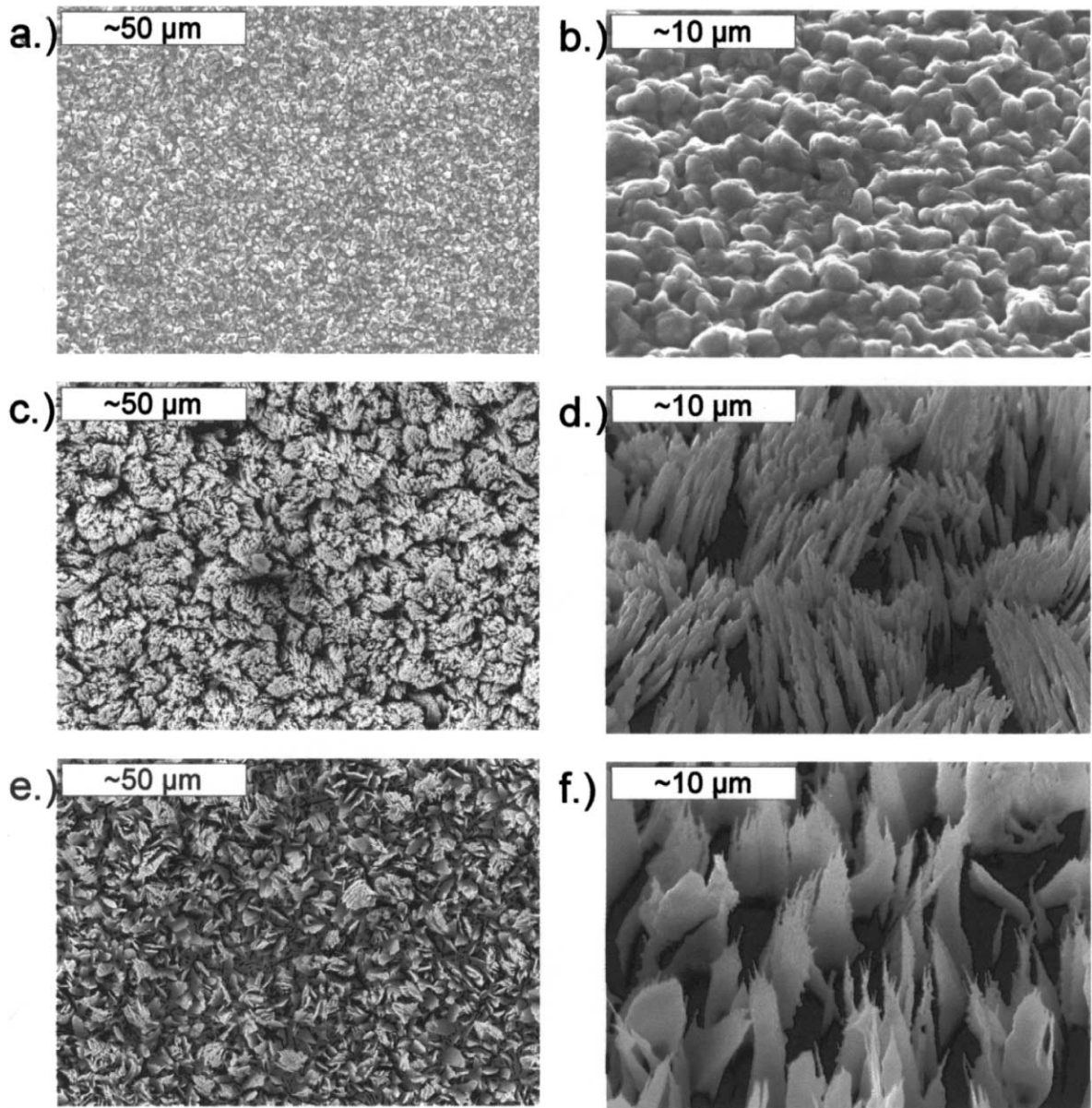Extremely different morphologies have been produced. The scale of morphologies ranged from stable

Fig. 8. Surface morphology of product layers grown at different temperatures (SEM). The films were prepared at 50°C (a,b), 100°C (c,d) and 160°C (e,f). The plasma was excited with a RF power of 50 W, $p = 1.00$ mbar, $U_{\text{bias}} = 65$ V. The reaction was performed for 1 h. Pictures (a,c,e) were taken with a magnification of 1000. The pictures (b,d,f) were taken under an angle of 45° with a magnification of 5000.

flat surfaces to needle-like and dendritic structures. The temperature dependence of the morphological development has been proven qualitatively. Nevertheless, there are still problems to be solved. Since the plasma is far from thermodynamic equilibrium, its behavior is extremely non-linear. This probably causes the sensitivity of the surface morphology to slight variations of the (geometric) boundary conditions. Thus, so far this study represents a promising step towards a systematic understanding of the kinet-

ics of metal oxidation in a plasma and of the morphological development of the resulting product layers.

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