

Deposition of amorphous chromium layers

Norbert Schröder · Birgit Sonntag · Waldfried Plieth

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Abstract Deposition of amorphous chromium-carbon layers is possible from a trivalent chromium electrolyte containing 0.6 mol/l formic acid. The formation of chromium/formic acid complexes inhibits the aging of the electrolyte and the oligomerization. Deposition of a 15–20 μm thick chromium film is possible with DC condition. Thicker films can be deposited with pulse plating using reversed pulse sequences and pulse lengths in the millisecond region. The optimized conditions concerning pulse current densities and pulse times were determined and the composition and morphology of the films investigated.

Introduction

Hard chromium layers deposited from hexavalent chromium electrolytes are, since invention of efficient plating baths, one of the most important plating processes [1, 2]. So far, deposition from trivalent chromium electrolytes is no alternative. The trivalent chromium electrolyte is difficult to handle because of long lasting and slow formation of chromium(III) polymer complexes and a reaction known as oligomerization, complexes formed by OH bridging. This leads to a limited lifetime of the electrolyte. Only thin films can be deposited and the properties of the deposit cannot be compared with the properties of the deposits from the

hexavalent chromium electrolyte. A review of the history of trivalent electrolytes was recently published [3].

A new stimulus for deposition from trivalent chromium electrolytes may come from deposition of amorphous chromium layers. Amorphous metal films are known from nickel phosphor and nickel boron alloy films. The layers have properties, which differ from crystalline films. These properties concern for instance hardness, ductility and in the case of nickel films magnetic properties. Amorphous films are formed, if the electrolyte contains chemicals like formic acid or hypophosphoric acid, sources for carbon atoms or phosphorus atoms stimulating formation of an amorphous structure [4]. Formation of amorphous chromium layers from hexavalent chromium electrolytes is difficult because the additional chemicals will be oxidized in the chromic acid. Therefore, experiments with trivalent chromium electrolytes were performed. The addition of additives has another effect because it is inhibiting formation of polymer complexes and the process of oligomerization. This paper is based on work of the PhD of one of the authors [5]. Selected results will be presented in this paper.

Experimental conditions

Three electrolytes were used for the experiments.

Electrolyte I: The basic electrolyte was prepared with a basic chromsulfate/sodiumsulfate mixture, $\text{Cr}_2(\text{OH})_2(-\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 10 \cdot \text{H}_2\text{O}$ (Chromitan B, Bayer AG), 120 g/l=0.2 mol/l, KCl, 250 g/l=3.35 mol/l, KBr, 15 g/l=0.13 mol/l, H_3BO_3 , 65 g/l=1.05 mol/l. KOH and HCl were used to adjust the pH to a value of 2.0.

Electrolyte II: Formic acid (28 g/l=0.61 mol/l), KOH (20 g/l=0.35 mol/l), and sodium dihexylsulfosuccinate (2 ml/l) as an additive were added to the electrolyte I. This electrolyte was used for deposition of chromium-carbon layers [6]. The pH was 2.1.

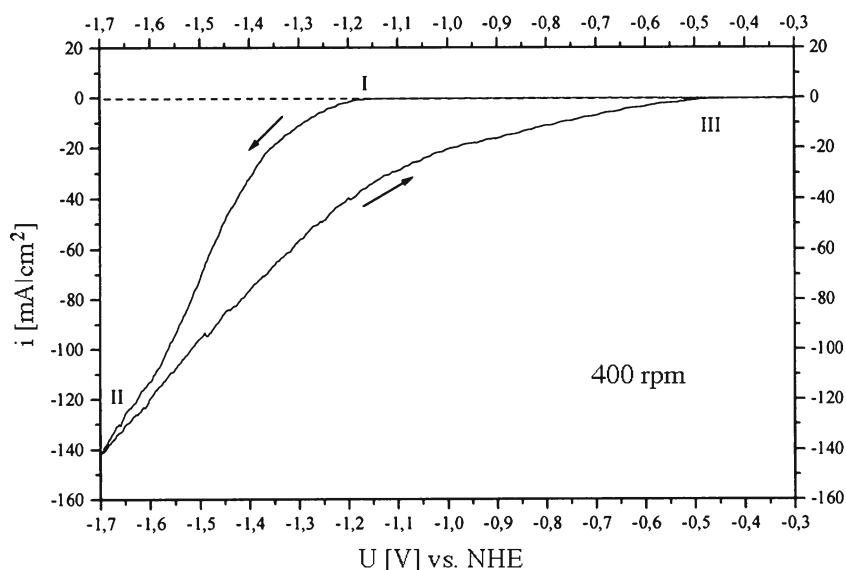
Electrolyte III: The electrolyte used for deposition of chromium-phosphorus layers was an ammonium electrolyte consisting of the basic chromsulfate/sodiumsulfate mixture,

W. Plieth (✉)
Physikalische Chemie und Elektrochemie,
Technische Universität Dresden,
01062 Dresden, Germany
e-mail: waldfried.plieth@chemie.tu-dresden.de

N. Schröder
ancosys GmbH, Pharmapark Radebeul,
Meissner Str. 191,
01445 Radebeul, Germany

B. Sonntag
Atotech Deutschland GmbH,
Erasmusstraße 20,
10553 Berlin, Germany

Fig. 1 Cyclic voltammogram with electrolyte I; scan rate 50 mV/s, rotation speed 400 rpm, $T=25\text{ }^{\circ}\text{C}$, $\text{pH}=2.0$



$\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 10 \cdot \text{H}_2\text{O}$ (Chromitan B), 120 g/l=0.2 mol/l, ammonium sulfamate, $\text{NH}_2\text{SO}_3\text{NH}_4$, 200 g/l=1.75 mol/l, NH_4Cl , 100 g/l=1.87 mol/l, KBr, 15 g/l=0.13 mol/l, H_3BO_3 , 65 g/l=1.05 mol/l, NaH_2PO_4 , 50 g/l=0.48 mol/l, sodium dihexylsulfosuccinate (2 ml/l). The pH was 3.0.

The films were deposited on zinc-coated steel plates usually used for Hull cell experiments (Carl Berghofer GmbH), the backside was isolated with “plating band” (3 M Scotch™ BRAND 471). The zinc layer was removed with 3 mol/l HCl. Afterwards, the plates were treated in Nonacid (Atotech Deutschland GmbH), 100 g/l. In this solution at room temperature, the electrodes were polarized

with 100 mA/cm², 10 s cathodic and 5 s anodic for 3 min (anodes were V2A steel plates). Afterwards, the plates were dipped into deionized water and for 30 s into 1 mol/l HCl. The anodes for the deposition were electrodes from pyrolytic graphite. The deposition was done galvanostatically or by pulse plating. A galvanostat (CAPP 25/20, Axel Åkermann) was used, which could be used for DC deposition as well as for pulse plating. The temperature at the deposition experiments was 48 °C, the temperature for optimized film properties.

Cyclic voltammetry was made in an analytical three-electrode cell (Metrohm). The working electrode was a glassy carbon-rotating disk electrode, the reference electrode a Hg/Hg₂SO₄/K₂SO₄ electrode (Metrohm, $E_{\text{SHE}}=$

Fig. 2 Cyclic voltammogram with electrolyte II containing formic acid; scan rate 50 mV/s, rotation speed 400 rpm, $T=25\text{ }^{\circ}\text{C}$, $\text{pH}=1.9$

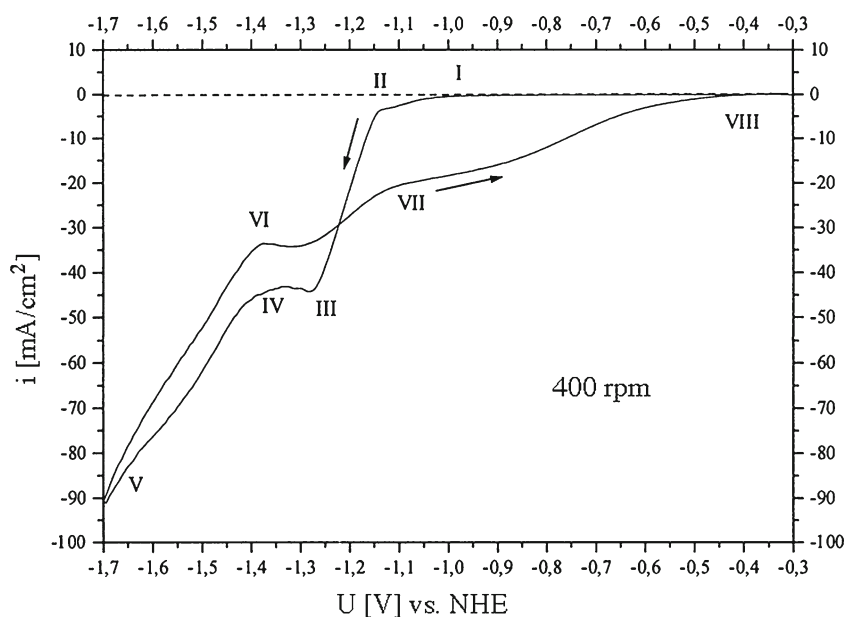
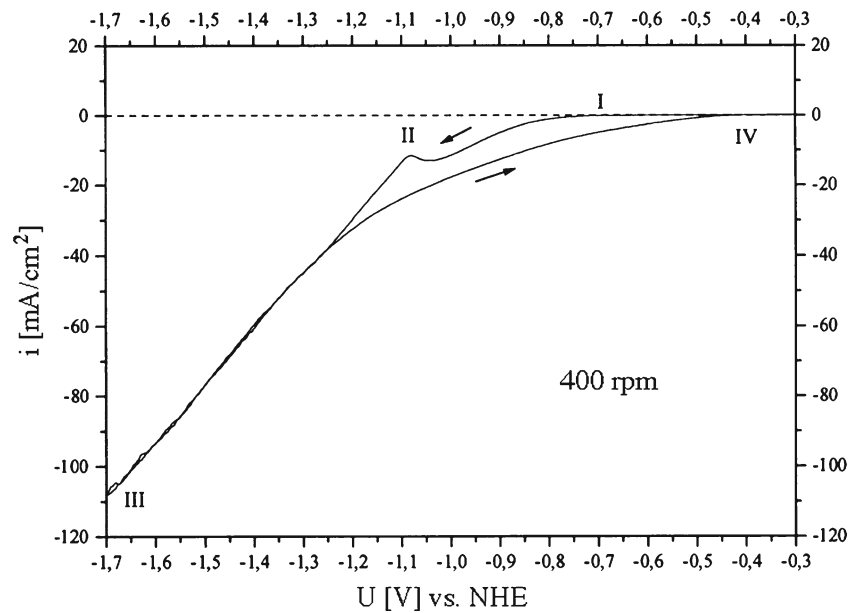


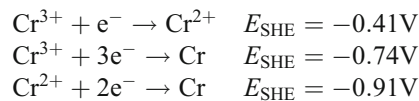
Fig. 3 Cyclic voltammogram with electrolyte III containing sodium hypophosphite; scan rate 50 mV/s, rotation speed 400 rpm, $T=25\text{ }^{\circ}\text{C}$, $\text{pH}=2.8$



650 mV at $25\text{ }^{\circ}\text{C}$). Potentiostat/Galvanostat was an Eg&G/ PAR 263A controlled by a PC. The temperature at the cyclic voltammetric measurements was $25\text{ }^{\circ}\text{C}$.

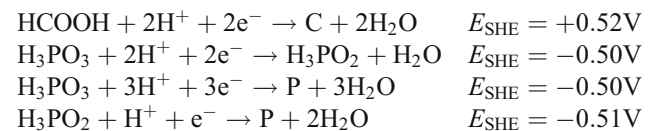
Kinetic investigations

For the following cyclic voltammetric investigation, a summary of the possible reduction potentials of chromium ions will be summarized.



In addition to the reduction of the chromium ions, the reduction of hydrogen ions to hydrogen is possible.

The reduction of the additives is described by the following equations.



The three electrolytes were investigated by cyclic voltammetry, the results with electrolyte I are shown in Fig. 1. The current starts to increase at -1.16 V with a high overvoltage.

Fig. 4 Glow discharge optical spectroscopy depth profile of the chromium–carbon film, DC deposited from electrolyte II, $T=48\text{ }\mu\text{m}$, film thickness $17\text{ }\mu\text{m}$

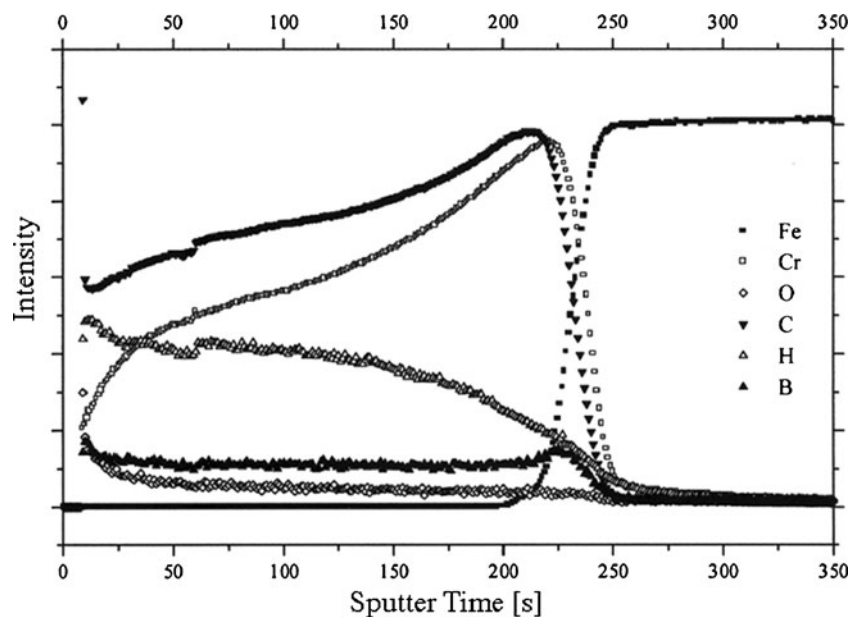
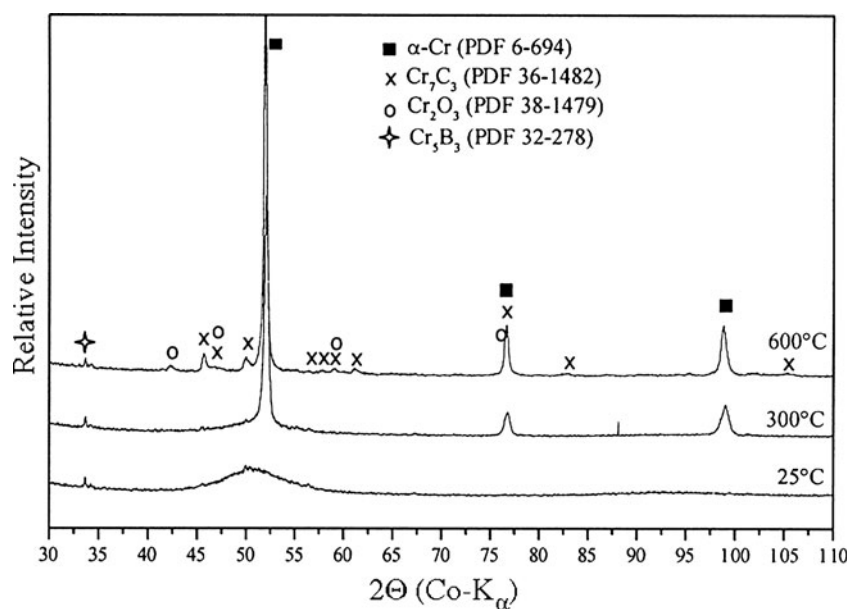


Fig. 5 X-ray diffraction pattern of the chromium–carbon film, DC deposited from electrolyte II, at 25 °C and after thermal treatment at 300 °C and at 600 °C



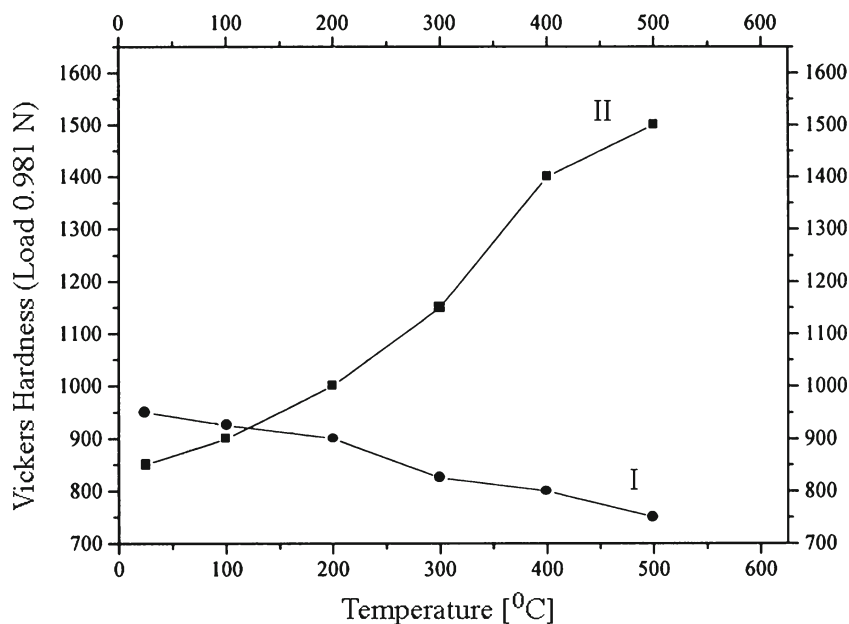
One observes hydrogen evolution and the formation of a dark film. It is assumed that reduction of Cr^{3+} ions to Cr^{2+} ions occurs. At the back scan, the current gets zero at -0.47 V.

Cyclic voltammograms with electrolyte II containing formic acid are shown in Fig. 2. Reduction starts at point I (-0.94 V). Formation of a metallic film begins at point II (-1.14 V) and is reaching a limiting current plateau at point III. A strong increase in current density occurs at point IV, maybe the start or increase of hydrogen evolution. In the back scan two plateaus are observed, below point VI (reduction of Cr^{3+} to Cr^0) and below point VII (reduction of Cr^{3+} to Cr^{2+}).

Cyclic voltammograms with electrolyte III containing sodium hypophosphite are shown in Fig. 3. The cathodic current starts at -0.68 V (point I). A black film is observed on the surface, the film was not investigated. At point II (-1.08 V) hydrogen evolution begins and on the surface a metallic film is formed. The chromium layer is of a metallic blue color.

The temperature in these kinetic experiments was 25 °C. The results describe the processes on the electrode surface at this temperature. The deposition experiments in the following paragraphs were made at 48 °C and this temperature was chosen for optimized deposition results. This restricts the transfer of the kinetic results to the deposition process.

Fig. 6 Hardness of the chromium-carbon film as function of temperature; Vickers hardness measured on the layer surface; I, conventional chromium layer, deposited from HEEF25 (Atotech Deutschland GmbH) at 55 °C; II, amorphous chromium/carbon layer, deposited with DC from electrolyte II at 48 °C



Deposition

DC deposition

Chromium–carbon layers were deposited from electrolyte II. Current density was 160 mA/cm², deposition time was 30 min, and temperature was 48 °C. The films were semi bright and thickness was 15–20 μm. Composition was 10.6 % carbon, 8.0 % boron, and 4.7 % oxygen (mass percent, energy-dispersive X-ray spectroscopy (EDX) analysis). A

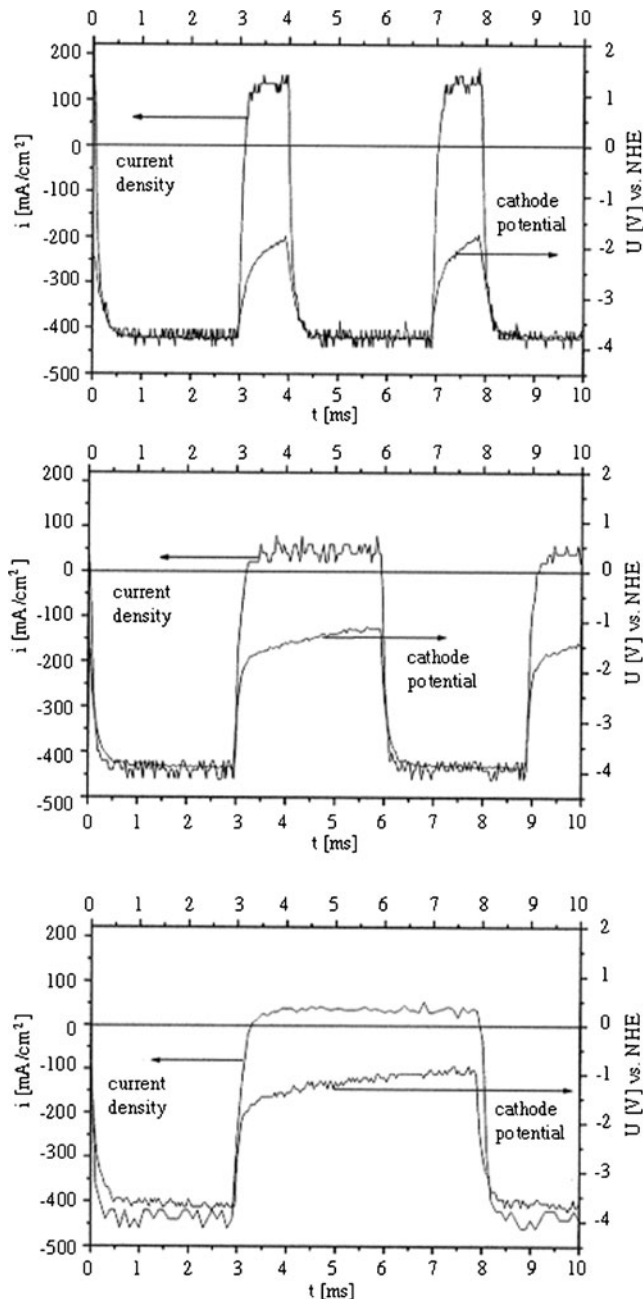


Fig. 7 Current-time and cathodic potential–time diagrams during reverse pulse deposition, electrolyte II containing formic acid

composition profile measured by glow discharge optical spectroscopy is shown in Fig. 4. The layers contained considerable amount of hydrogen. The film was amorphous as proofed by X-ray diffraction, shown in Fig. 5. The film after thermal treatment gets crystalline with formation of chromium carbide, chromium oxide and chromium boride. The film has microcracks. The hardness of the film after a thermal treatment as function of temperature is shown in Fig. 6.

Chromium–phosphorus layers deposited from electrolyte III were rough, had macrocracks and a tendency for dendrite formation. Composition was 14.8 % phosphorus, 9.6 % boron, and 9.3 % oxygen (mass percent, EDX analysis). The phosphorus blocked the chromium deposition. The film thickness after 30 min deposition time ($i=260$ mA/cm²) was limited to 3–4.5 μm.

Reverse pulse deposition

The problem with deposition from a trivalent chromium electrolyte is the limited layer thickness. The stop of the deposition is explained by the formation of chromium(III) complexes catalyzed by the chromium(II) ions formed in front of the cathode. The formation of chromium(III) complexes can be inhibited by some compounds like formic acid.

Another possible control of complex formation at the cathode is pulse plating [7]. The interruption of the deposition current limits the amount of chromium(II) ions formed at the cathode. Experiments were made with single pulses and with reversed pulses. Results of experiments with pulse duration in the region of seconds gave similar layer properties then DC deposition. Different properties were obtained with pulse duration in the region of milliseconds. Results are shown in Figs. 7, 8, 9 and 10.

With pulse deposition, the number of experimental parameters is much larger then with DC deposition. Each

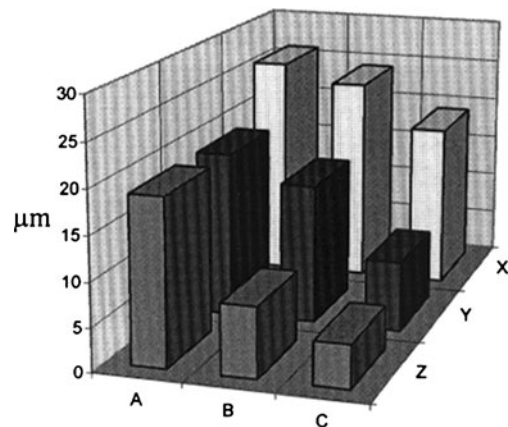


Fig. 8 Influence of pulse duration and current density on the layer thickness; A $t_a=1$ ms, $i_a=140$ mA/cm²; B $t_a=3$ ms, $i_a=47$ mA/cm²; C $t_a=5$ ms, $i_a=28$ mA/cm²; X $t_c=3$ ms, $i_c=417$ mA/cm²; Y $t_c=5$ ms, $i_c=250$ mA/cm²; Z $t_c=7$ ms, $i_c=176$ mA/cm², $T=48$ °C

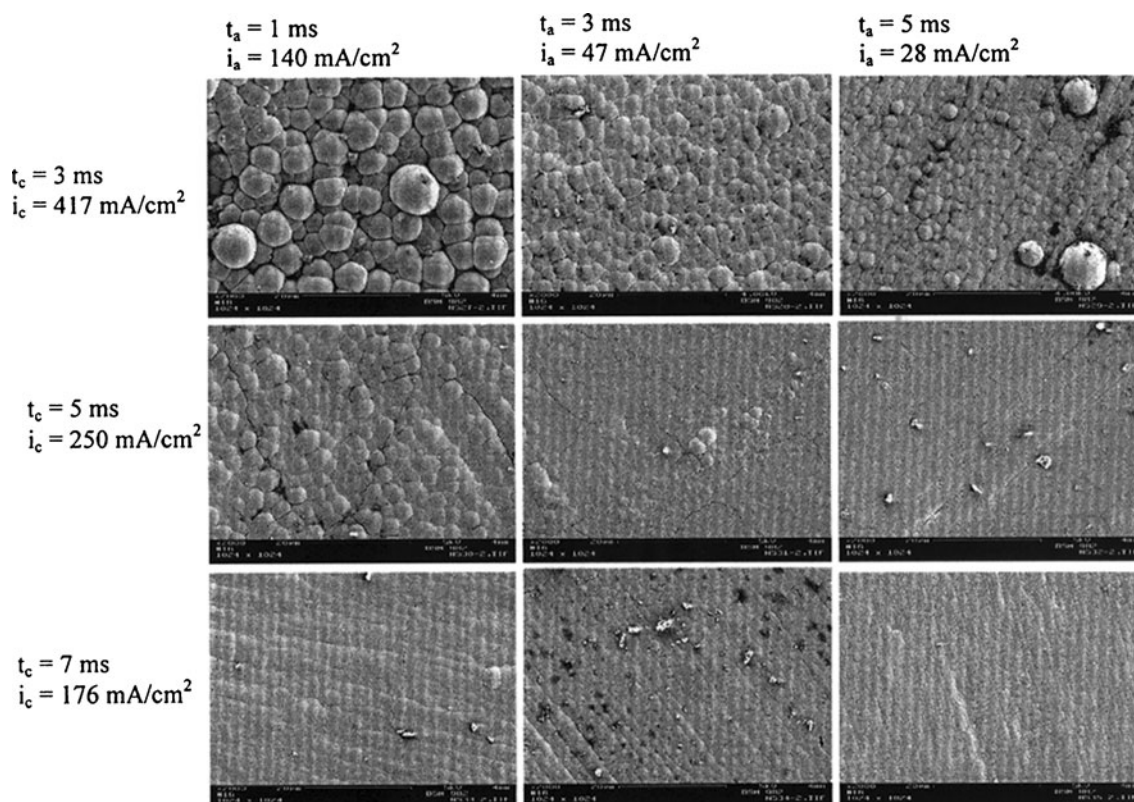


Fig. 9 Influence of pulse duration and current density on the layer morphology by SEM surface images, magnification 2000, $T=48\text{ }^{\circ}\text{C}$

pulse is controlled by the pulse current density, the pulse time, and the pulse charge. Deposition with reversed pulsing needs these parameters twice. The sum of cathodic and anodic pulse time is the cycle time. Another experimental parameter is the temperature of the electrolyte.

To reduce the number of experiments, Taguchi developed a method of statistical planning of experiments [8, 9]. The method is using factors describing the deviation from the statistical scattering of experimental values (control factors) and from the expected results (signal factors). Interactions between the experimental parameters limit the number of experiments. The number of independent experiments is plotted in so-called orthogonal arrays versus the experimental parameters. The method was applied and the ratio of pulse charges Q_a/Q_c , the anodic pulse time t_a and the temperature of the electrolyte T were chosen as experimental parameters. The temperature was varied between 25 and 45 $^{\circ}\text{C}$.

The results gave layer thicknesses of 20–50 μm and Vickers hardness values $\text{HV}_{0.1}$ of 500–600. Higher temperature of the electrolyte gave better optical properties. For further experiments, the temperature of 48 $^{\circ}\text{C}$ was chosen.

To study the influence of current density and morphology on the layer morphology, the cathodic and anodic pulse charge was kept constant with $Q_c+Q_a=1,598\text{ As}$ and $Q_a/Q_c=1/9$. The number of cycles was 180,000. The cathodic pulse time was $t_c=3, 5, \text{ and } 7\text{ ms}$, the anodic pulse time was

$t_a=1, 3, \text{ and } 5\text{ ms}$. The corresponding current densities were $i_c=417, 250, \text{ and } 176\text{ mA/cm}^2$ and $i_a=140, 47, \text{ and } 28\text{ mA/cm}^2$. The electrochemical processes in the reverse pulse plating were studied by measurements of current–time and of the cathodic potential–time diagrams (Fig. 7).

The diagrams in Fig. 7 show that the potential of the cathode stays in the region of hydrogen development even during the anodic pulse. The reduction of hydrogen ions is not stopped. But deposition of chromium during the anodic pulse is not possible. The anodic current in the anodic pulse is connected with the new charging of the double layer.

The influence of the varied experimental parameters on the layer thickness is shown in Fig. 8. The layer thickness increases with increasing cathodic current density. This is an expected result. Otherwise, the layer thickness decreases with increasing anodic pulse time. That means the recharging of the double layer has an inhibiting effect on the chromium deposition. The influence of pulse duration and current density on the layer morphology is shown with SEM images of the surface in Fig. 9 and with SEM images of the cross-section in Fig. 10.

The results of these experiments demonstrate that the deposition of chromium layers from trivalent chromium electrolytes with reverse pulse plating is possible with layer properties comparable with layers from hexavalent electrolytes.

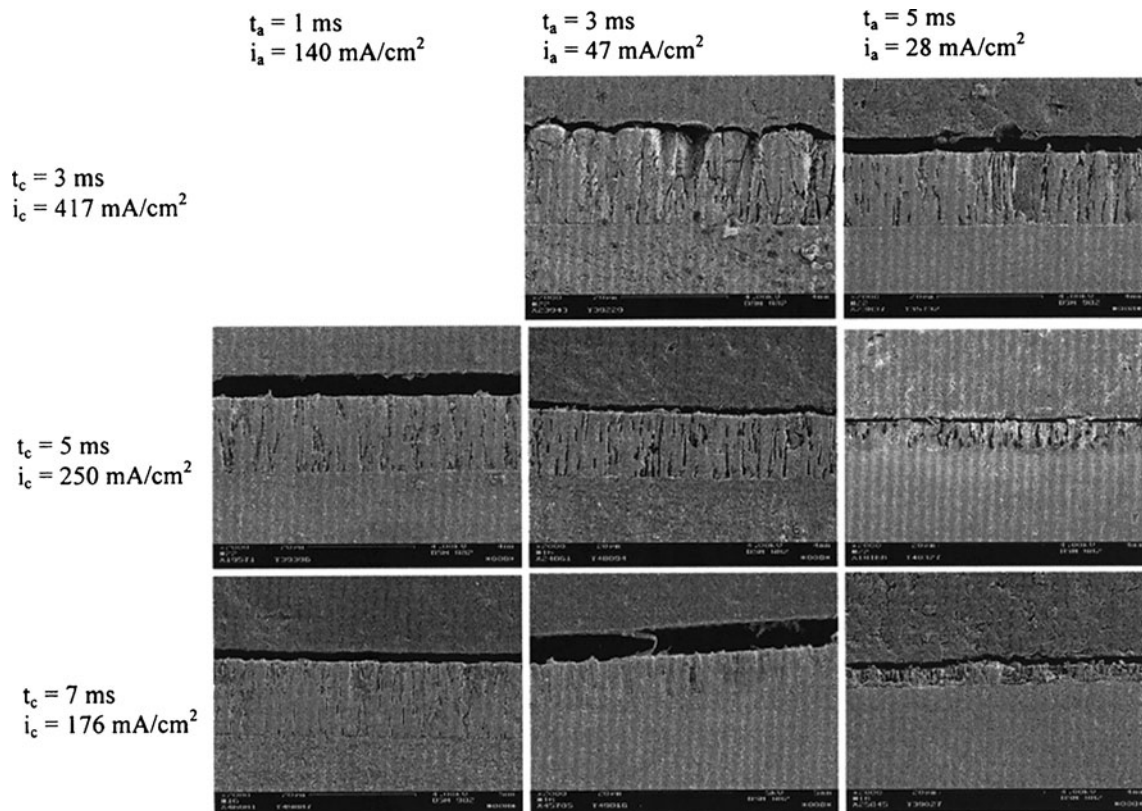


Fig. 10 Influence of pulse duration and current density on the layer morphology by SEM images of the cross-section; magnification, $\times 2,000$; $T=48\text{ }^\circ\text{C}$

Reverse pulse plating with cathodic double pulse

The incorporation of hydrogen was not reduced by the reverse pulse deposition if compared with layers DC deposited. Different results were obtained by reverse pulse plating with cathodic double pulses. An electrolyte temperature of $48\text{ }^\circ\text{C}$ was chosen, the deposition time was 30 min, the thickness of the deposited film was $32\text{ }\mu\text{m}$. The pulse parameters were $t_{c1}=2\text{ ms}$, $i_{c1}=250\text{ mA/cm}^2$, $t_{c2}=11\text{ ms}$, $i_{c2}=103\text{ mA/cm}^2$, $t_a=1\text{ ms}$, $i_a=160\text{ mA/cm}^2$.

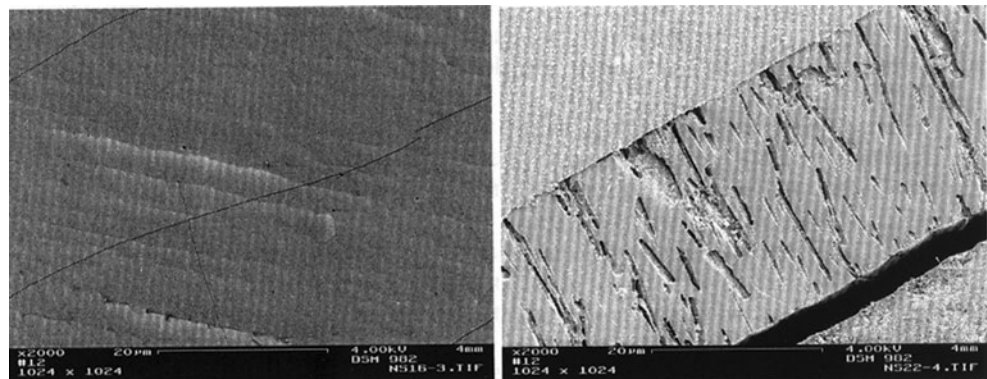
SEM images are shown in Fig. 11. The largest difference to the former examples, the hydrogen content was reduced,

if compared to reverse pulse plating and DC deposition. This is shown in Fig. 12.

Conclusion

The results of this investigation show the complex problems involved in chromium deposition from trivalent chromium electrolytes. The trivalent chromium electrolyte is modified by additives like formic acid and thicker films of amorphous chromium/carbon films can be deposited. Additionally, improvement is achieved by applying pulse plating. Reverse

Fig. 11 Reverse pulse plating with cathodic double pulse, top view, and cross-section, deposition time 30 min, $T=48\text{ }^\circ\text{C}$, thickness $32\text{ }\mu\text{m}$; magnification, $\times 2,000$



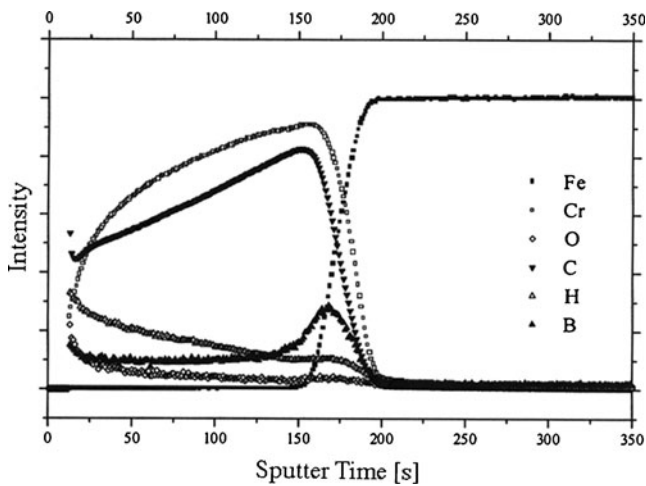


Fig. 12 Reverse pulse plating with cathodic double pulse, glow discharge optical spectroscopy analysis, deposition time 30 min, $T=48\text{ }^{\circ}\text{C}$; thickness, $18\text{ }\mu\text{m}$

pulse plating was applied. The optimization of the pulse parameters was obtained by application of the statistical planning of experiments with the method suggested by Taguchi.

The last deposition procedure was reverse pulse plating with cathodic double pulse. The hydrogen content of the film was reduced by this method. The trivalent chromium electrolyte for deposition of chromium–carbon films is suited to deposit amorphous chromium layers with improved thickness and layer properties.

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