



Machbarkeitsstudie zu geeigneten Kandidaten für die Herstellung von CRM für die Bestimmung von Wasserstoff in Festkörpern

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Overview on analytical methods for the analysis of hydrogen in solid samples

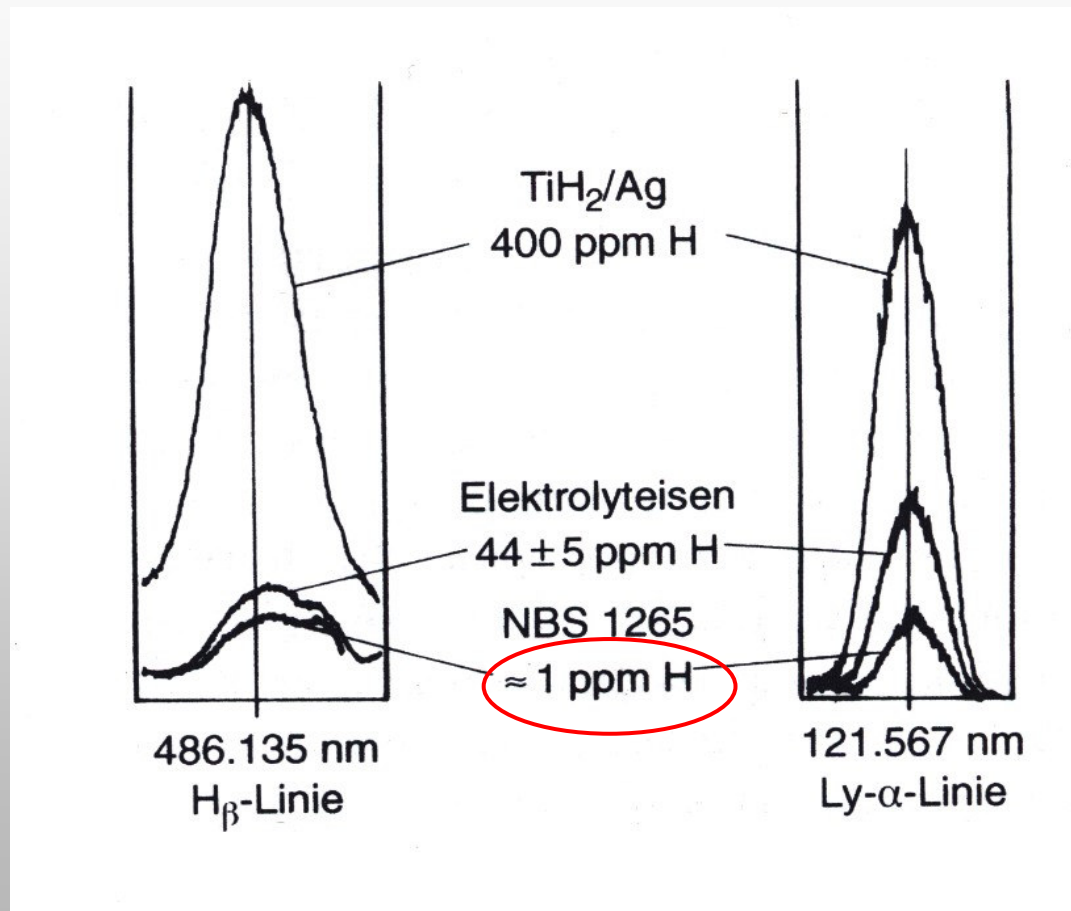


Analytical Method	Detection of H	Quantification of H	Limitations
HotE	√	√	no local information (i.e., no depth profiles)
NRA	√	√	analysed depth of up to only 1-2 μm $\text{LoD}_H \sim 10 \text{ ppm}$
ERDA	√	√	"
SIMS	√	—	lack of H-CRM, thin layers
GD-OES	√	—	lack of H-CRM

(www.comar.bam.de)



Analytical figures of merit in GD-OES: Limit of Detection (LoD) of H



GD-OES-Lines for Hydrogen Detection

(*Werkstoffanalytische Verfahren*, H.-J. Hunger, Ch. 12: *Glimmentladungsspektroskopie*, 1995).

Analytical figures of merit in GD-OES: Limit of Detection (LoD) of H



1265A certificate.pdf - Adobe Reader

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1 / 3 66,7% Suchen

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1265a

Electrolytic Iron

This Standard Reference Material (SRM) is in the form of disks 32 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.*

Element	Percent by Weight	Element	Percent by Weight
Carbon	0.0067 ± 0.0003	Cobalt	0.007 _o
Manganese	.0057	Titanium	(.0001)
Phosphorus	.0011 ± .0001	Arsenic	(.0002) ^b
Sulfur	.0055 ± .0003	Aluminum (total)	(.0007)
Silicon	.008 _o	Boron	.00013
Copper	.0058	Lead	.000015
Nickel	.041	Iron (by diff.)	99.9
Chromium	.0072		
Vanadium	.0006		
Molybdenum	.0050		

*This material also is available in the form of chips, SRM 365, for use in chemical methods of analysis; rods SRM 1099, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 665, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

^bValues in parentheses are not certified as they are based on the results from a single laboratory or analytical method.

CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

Renewals of the "1200 series", 1261a-1265a, were prepared from the same ingots used for the original series, but from adjacent positions within the ingots. Little or no change in elemental composition was observed by comparison analysis utilizing several analytical techniques: optical emission spectrometric analysis, J.A. Norris and D.E. Brown; x-ray fluorescence analysis, P.A. Pella and J.R. Sieber; combustion-infrared, B.I. Diamondstone.

The overall direction and coordination of the technical measurements at NIST leading to certification were performed under the direction of K.F.J. Heinrich, O. Menis, B.F. Scribner, J.I. Shultz, and J.L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.E. Michaelis and W.P. Reed.

June 12, 1989
Gaithersburg, MD 20899
(Revision of certificate dated 2-24-81)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not certified may be of importance in the use of the material. Although these are not certified, upper limit values are presented in the following table for the remaining elements.

Elements Detected (ppm by weight)

Element	Upper Limit	(Estimated value)	Method
Tungsten	<1	(0.4)	Neutron activation
Tin	<2	(2)	Spark source mass spectrometry
Antimony	<0.5	(< 0.1)	Spark source mass spectrometry
Silver	<0.2	(0.02)	Spark source mass spectrometry
Zinc	<3	(< 1)	Atomic absorption
Nitrogen	<20	(~ 11)	Distillation-photometric
Germanium	<50	(~ 14)	Spark source mass spectrometry
Oxygen	<20	(62)	Vacuum fusion
Hydrogen	< 5	(1)	Vacuum fusion

Elements Sought But Not Detected (ppm by weight)

Element	Upper Limit	Method
Tantalum	<0.5	Neutron activation
Zirconium	<0.1	Spark source mass spectrometry
Antimony	<0.5	Neutron activation
Bismuth	<0.1	Spark source mass spectrometry
Calcium	<0.1	Atomic absorption
Magnesium	<0.2	Atomic absorption
Selenium	<0.1	Spark source mass spectrometry
Tellurium	<0.1	Spark source mass spectrometry
Cerium	<0.05	Spark source mass spectrometry
Lanthanum	<0.05	Spark source mass spectrometry
Praseodymium	<0.05	Spark source mass spectrometry
Gold	<0.02	Neutron activation
Hafnium	<0.2	Spark source mass spectrometry
Neodymium	<0.05	Spark source mass spectrometry

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Institute of Standards & Technology. The contract was made possible by a grant from the American Iron and Steel Institute.

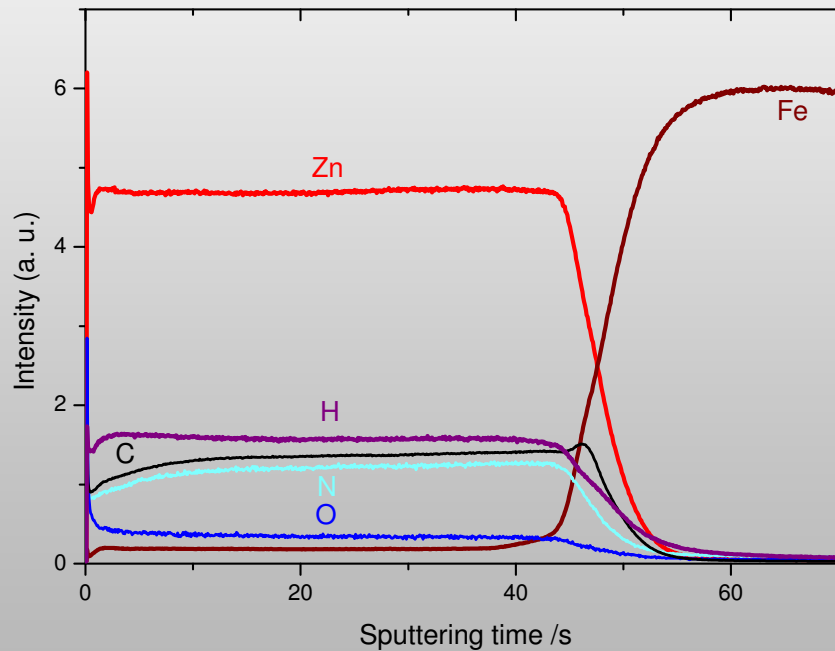
The ingots were processed by Carpenter Technology Corporation to provide material for the highest possible homogeneity. Following acceptance of the composition based on NIST analysis, selected portions of the ingot material were extensively tested for homogeneity at NIST by J.R. Baldwin, D.M. Bouchette, S.D. Rasberry, and J.L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

-2-

216,4 x 279,4 mm

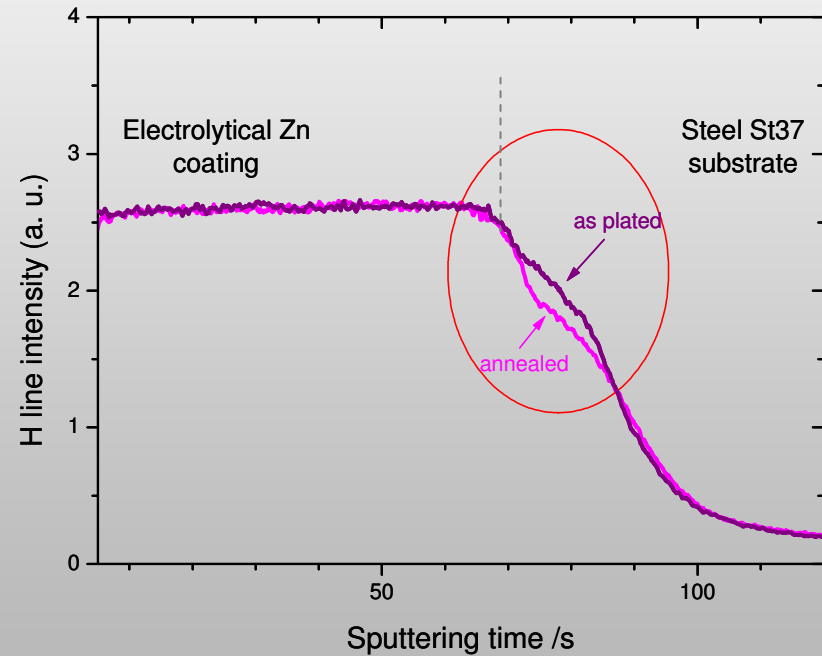


GD-OES element depth profile



$\varnothing_{\text{GD-anode}} = 4 \text{ mm}$; $V_{\text{dc}} = 800 \text{ V}$; $p = 700 \text{ Pa}$;
 Zn I 330.2 nm; Fe I 371.9 nm; H I 121.5 nm; C I 156.1 nm; N I 149.2 nm;
 O I 130.2 nm; Ar I 415.8 nm

H depth profile before and after heat treatment



$\varnothing_{\text{GD-anode}} = 4 \text{ mm}$; $V_{\text{dc}} = 700 \text{ V}$; $I_{\text{dc}} = 20 \text{ mA}$;
 H I 121.5 nm



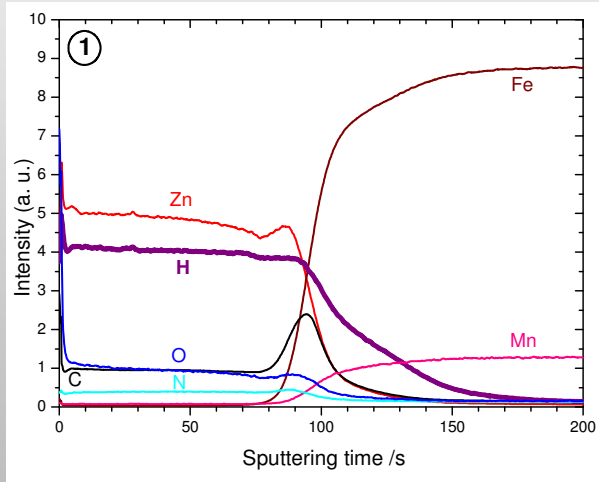
- ▶ **Homogeneity** of the H concentration in the *coating* (as an alternative to *bulk*)
 - lateral
 - in-depth

- ▶ **Stability** (!) of the H concentration over longer periods of time (i.e. years)

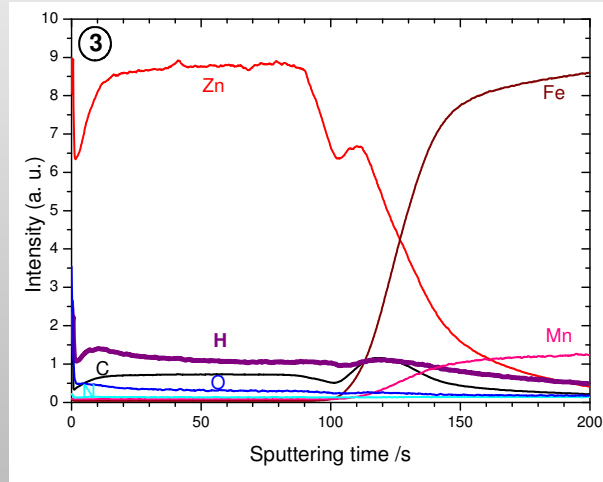
Coating as candidates for H-CRM (CRC): (i) Electroplated Zn(H) on steel



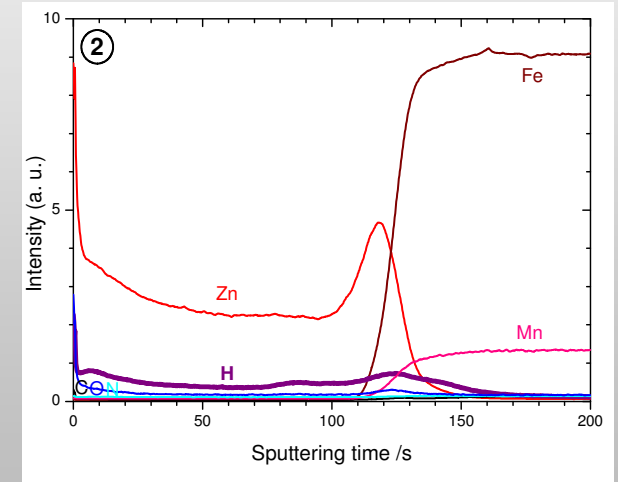
Cyanide-free alkaline Zn electrolyte,
low additive concentration



Cyanide Zn electrolyte,
without additives



Acid Zn electrolyte,
without additives



Electroplated Zn(H) on steel; Determination of the H concentration by ERDA & NRA; Stability tests

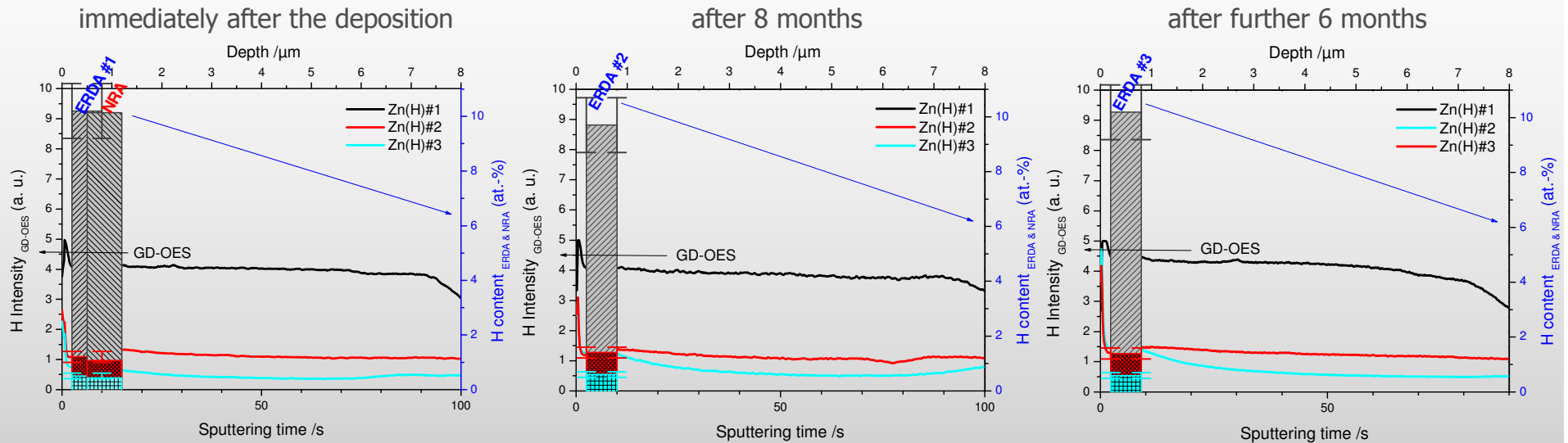
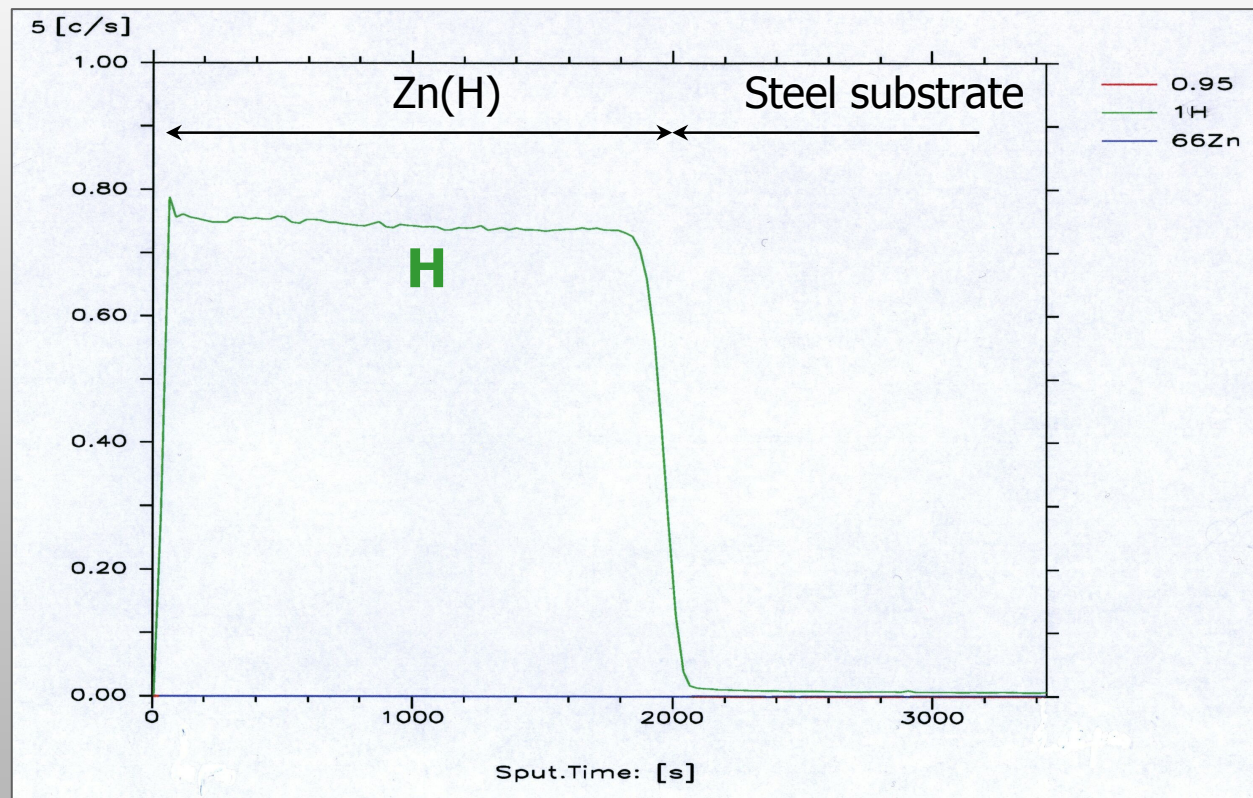


Table 1 Stability tests of the hydrogen concentration in at.-% in three electroplated zinc coatings determined by ERDA.

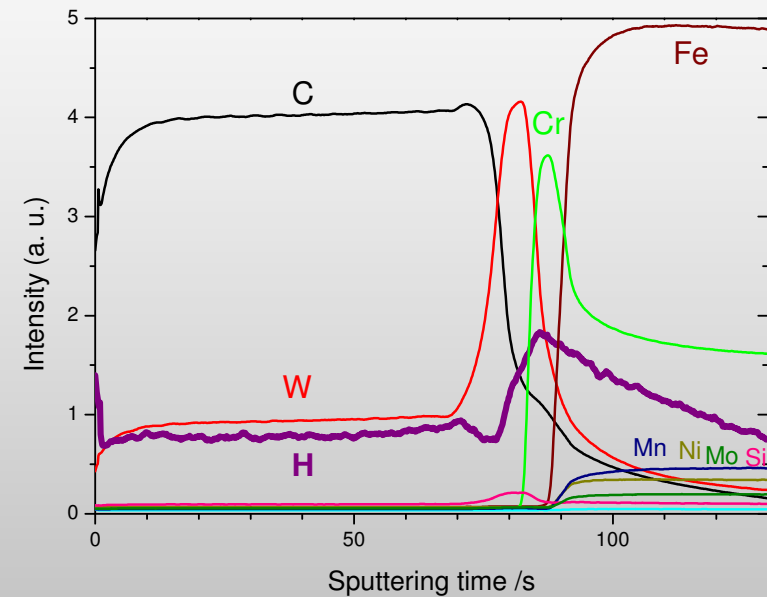
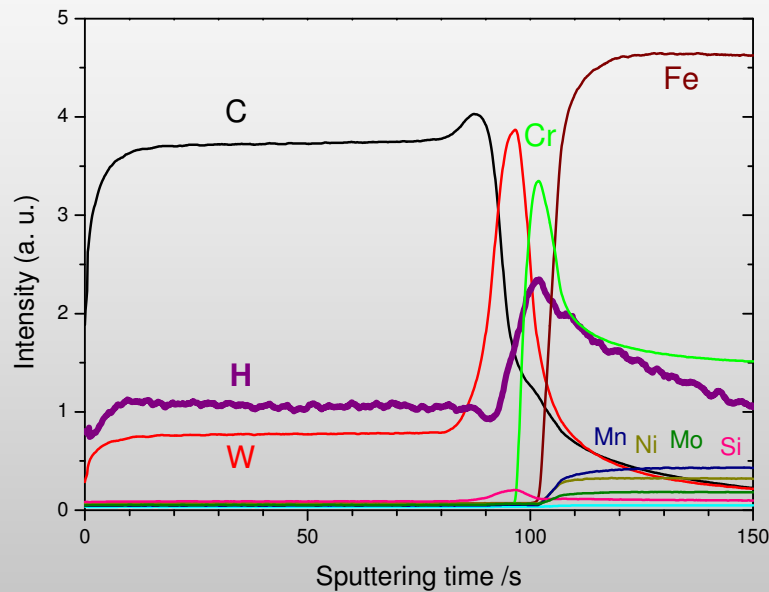
Sample	immediately after the deposition	after 8 months	after further 6 months
Zn(H) #1	10.2 ±1.0	9.7 ±1.0	10.2 ±1.0
Zn(H) #2	1.2 ±0.2	1.4 ±0.2	1.4 ±0.2
Zn(H) #3	0.5 ±0.1	0.6 ±0.1	0.6 ±0.1



Electroplated Zn(H) on steel;
Homogeneity tests;
SIMS depth profile of H, $\varnothing_{PI}=10 \mu\text{m}$



Coating as candidates for H-CRM (CRC): (ii) Carbon-rich hard coatings, WC(H) / steel



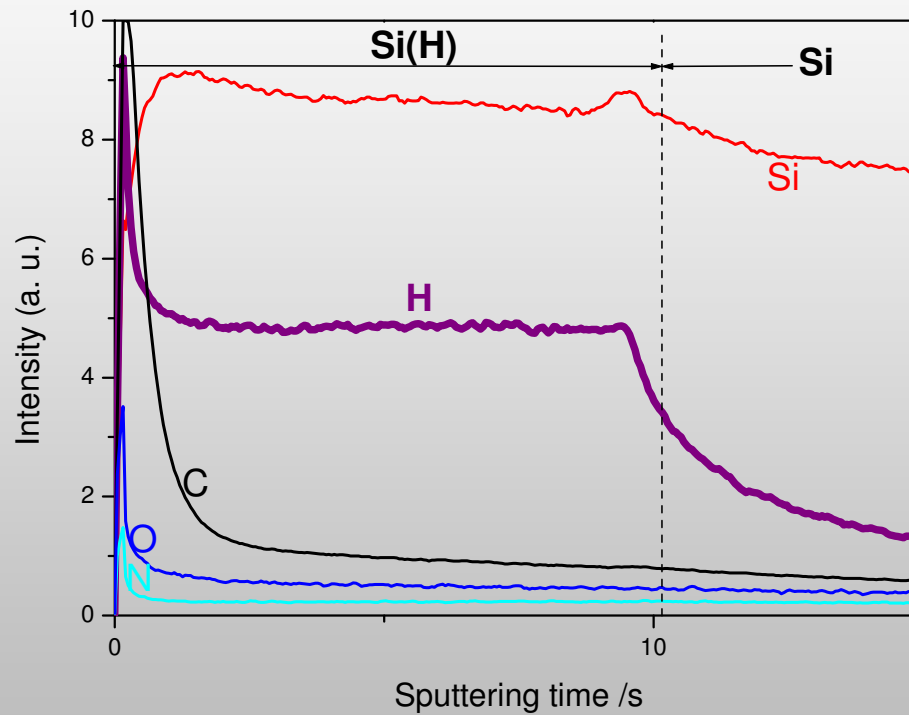
The corresponding hydrogen concentrations found by ERDA are 22.1 ± 2.0 and 18.4 ± 2.0 at.-%.

$\varnothing_{\text{GD-Anode}} = 4 \text{ mm}$; $V_{\text{dc}} = 700 \text{ V}$; $I_{\text{dc}} = 20 \text{ mA}$;

C I 156,1 nm; W I 400,8 nm; H I 121,5 nm;

Fe I 371,9 nm; Cr I 425,4 nm; Mn I 403,4 nm; Ni I 349,2 nm; Mo I 386,4 nm; Si I 288.1 nm

Coating as candidates for H-CRM (CRC): (iii) Amorphous Si layers, a:Si(H) / Si



$\varnothing_{\text{GD-anode}} = 4 \text{ mm}$; $V_{\text{dc}} = 700 \text{ V}$; $I_{\text{dc}} = 20 \text{ mA}$;
H I 121.5 nm



Coating as candidates for H-CRM (CRC): (iii) Amorphous Si layers

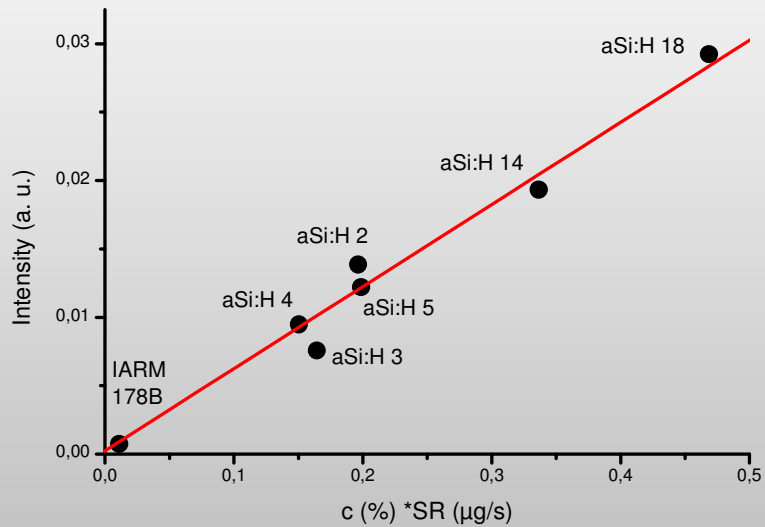


Table 2 Samples used for the calibration curve in Fig. 4

Sample	Sputter factor SR (µg/s)	H (at.-%)	H (mass-%)
aSi:H 2	0.40	12.14	0.493
aSi:H 3	0.34	11.89	0.482
aSi:H 4	0.31	12.06	0.490
aSi:H 5	0.43	11.54	0.466
aSi:H 14	0.57	14.23	0.592
aSi:H 18	0.56	18.80	0.824
IARM 178B	1.15	0.144	0.003

$\varnothing_{\text{GD-anode}} = 4 \text{ mm}$; $V_{\text{dc}} = 1000 \text{ V}$; $I_{\text{dc}} = 18 \text{ mA}$ (IFW Dresden)

H I 121.5 nm

Coating as candidates for H-CRM (CRC): (iii) Amorphous Si layers



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http://www.bam.de/de/fachthemen/referenzmaterialien/index.htm

BAM Fachthemen | Referenzmaterialien

Referenzmaterialien

Referenzmaterialien (RM) sind der Schlüssel chemischer Analysen und technischer Messungen.

Leitfaden für die Entwicklung von BAM-Referenzmaterialien


In der BAM sind zertifizierte Referenzmaterialien für die Bestimmung von Schwermetallen und Quellungsmessungen vertrieben.

COMAR

BAM Fachthemen | Referenzmaterialien | RM Aktuell - Windows Internet Explorer
http://www.bam.de/de/fachthemen/referenzmaterialien/rm_aktuell

Wasserstoff in einer amorphen Siliciumschicht BAM-S110

Bei dem Referenzmaterial **BAM-S110** handelt es sich um eine wasserstoffhaltige, amorphe Siliciumschicht auf Siliciumsubstrat mit zertifiziertem Wasserstoffanteil X_H . Es ist für den Einsatz als Kalibrierprobe für die zerstörende Wasserstoffanalytik mittels Glimmladungs-Spektrometrie (GDOES) und Sekundärionen-Massenspektrometrie (SIMS) vorgesehen.



Wasserstoff in einer amorphen Siliciumschicht BAM-S110

[BAM-S110 report](#) (PDF, 100 KB)

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2007-12-18



Coating as candidates for H-CRM (CRC): (iii) Amorphous Si layers



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1 / 2 66,6% Suchen

Bundesanstalt für Materialforschung und -prüfung
Zertifiziertes Referenzmaterial
BAM-S110
Wasserstoff in einer amorphen Siliciumschicht
Zertifizierter Wert

Wasserstoffanteil X_H [%]**	Erweiterte Unsicherheit $U(X_H)$ * [%]**
11,9	0,8

* Unsicherheit, erweitert mit dem Faktor $k = 2$, beinhaltend die Unsicherheit der Charakterisierung (ausgedrückt als Standardabweichung des Mittelwertes der Mittelwerte des Wasserstoffgehaltes der drei beschriebenen Substrate (Wafer)), den Inhomogenitätsbeitrag nach ISO Guide 35, sowie den Unsicherheitsbeitrag der Rückführung der Messergebnisse auf den Urstoff 3-Phenylalanin
** Teilchenanzahlanteil nach DIN 1310 (früher auch als at.% bezeichnet)

Anwendungsbereich
Bei dem Referenzmaterial BAM-S110 handelt es sich um eine wasserstoffhaltige, amorphe Siliciumschicht auf Siliciumsubstrat mit zertifiziertem Wasserstoffanteil X_H . Es ist für den Einsatz als Kalibrierprobe für die zerstörende Wasserstoffanalytik mittels Glimmentladungs-Spektrometrie (GDOES) und Sekundärionen-Massenspektrometrie (SIMS) vorgesehen.

Probenform
Das Referenzmaterial BAM-S110 besteht aus einem mit amorphen Silicium beschichteten Siliciumeinkristallsubstrat mit einer Kantenlänge von 18 mm x 18 mm x 0,5 mm. Die Schichtdicke ist größer 1 µm.

Ende der Nutzungsdauer
Das ZRM ist mindestens bis April 2010 nutzbar.
Damit ist nicht ausgeschlossen, dass der Wert des Stoffmengenanteils Wasserstoff des Referenzmaterials auch nach diesem Zeitraum weiterhin dem Zertifikat entspricht.

BAM-S110 Seite 1 von 2

Hinweise zur korrekten Handhabung
Die Proben sollten nur mit einer Teflonpinzette gehandhabt werden. Eine Oberflächenkontamination ist auszuschließen.

Hinweise zur korrekten Lagerung
Die Lagerung soll unter normalen Bedingungen erfolgen.

Zertifizierungsbericht
U. Reinholz, H.-P. Weise, K.-W. Brzezinka, W. Bremser, „BAM-S110: Wasserstoff in einer amorphen Siliciumschicht“, Berlin, 2007

Bundesanstalt für Materialforschung und -prüfung (BAM)
12200 Berlin, 2007-09-25

Abteilung I Analytische Chemie; Referenzmaterialien	Fachgruppe I.3 Strukturanalytik; Polymeranalytik
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Prof. Dr. rer. nat.
U. Panne

Dr. rer. nat.
A. Thünemann

Verkauf des Materials:

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BAM-S110 Seite 2 von 2



At least three classes of reference coatings as successful candidates for upcoming certification of the H concentration:

- *Electrolytically Zn(H) / steel*
- *Carbon-rich hard coatings, WC(H) / steel*
- *Amorphous Si layers, a:Si(H) / Si*

- V.-D. Hodoroaba, D. Klemm, U. Reinholz, E. Strub, J. Röhrich, W. Bohne, V. Hoffmann and K. Wetzig, Potential candidates of Certified Reference Material for determination of hydrogen concentration with Glow Discharge Optical Emission Spectrometry (GD-OES) - a feasibility study, *J. Anal. At. Spectrom.*, 2008, **23**, 460 – 462.