Spectroscopic Ellipsometry as in-situ diagnostic tool for the avoidance of compound layer formation during plasma nitriding

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ABSTRACT

Plasma nitriding was studied in detail in-situ on steel substrates (material code: 1.7225) via spectroscopic ellipsometry in order to avoid the formation of a compound layer. The aim was to identify the compound layer formation by analyzing differences in the dielectric function.It turned out that the temporal evolutions of the ψ signal at 450 nm and the position of the 3rd oscillator (L32), as evaluated by an ellipsometer model, were best suited for on-line control. A so called transition region was found attributed to the formation of the compound layer. Therefore, a variety of experiments were performed where the nitriding process was stopped at different durations of treatment within the transition region. The existence of the compound layer was proofed by reaction of copper sulphate with treated substrates. To get more information about the phase composition several X-ray diffraction (XRD) measurements were carried out. It turned out that the compound layer composition is iron nitride consisting of only Fe_4N. Atomic force microscopy (AFM) images revealed an increase of the surface roughness in the course of the nitriding step especially within the transition region.

Further a CLC (closed loop control) system was developed to monitor and automatically control the nitriding process to avoid compound layer formation.

RESULTS

On-line monitoring of the nitriding process

- certain feature of ellipsometer signal attributed to compound layer (Fe_4N) formation
- nitriding step divided into different time stages
  1. onset
  2. plateau
  3. slope
  4. minimum
  5. ascent

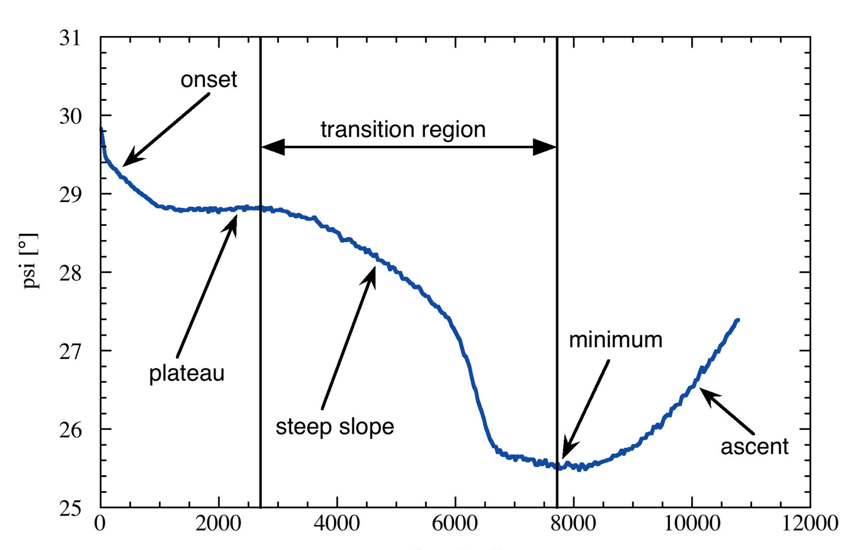


Fig. 3: Kinetic measurement of Ψ during the nitriding step.

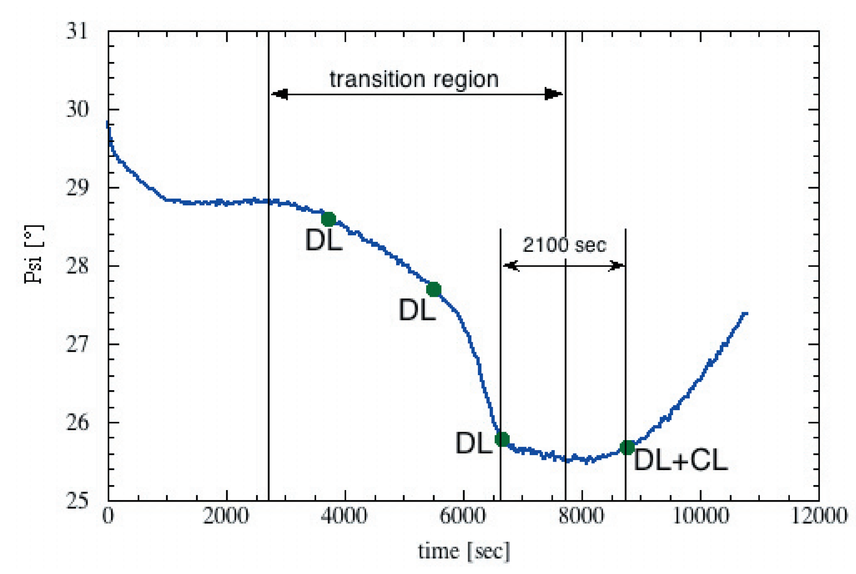
- signal between plateau and minimum

↓

transition region

↓

beginning of compound layer formation



***DL**: diffusion layer (N_2 interstitially dissolved.*
***CL**: compound layer (N_2 forms chemical compound Fe_4N)*

Fig. 5: Kinetic measurement of Ψ at 450 nm. The green dots represent samples interrupted after different nitriding durations and varified by the copper sulphate solution.

- **AFM (Atomic force microscopy)** measurements exhibited a drastical increase of the surface roughness within the transition region due to recrystallization and nitride formation

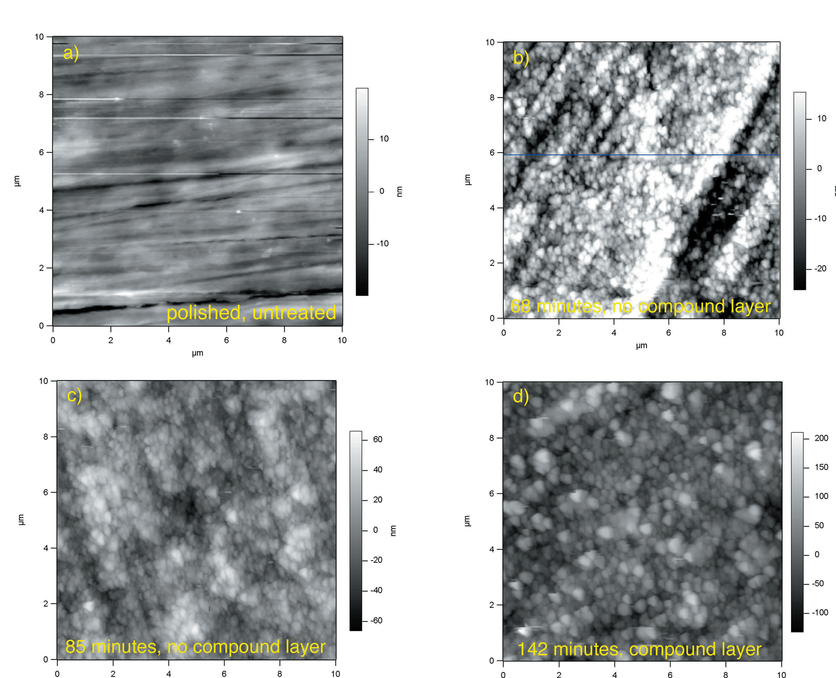


Fig. 6: AFM-images of the surface morphology of nitrided steel substrates with different nitriding times. a) untreated; b) 68 minutes; c) 85 minutes; d) 142 minutes (with compound layer)

- **copper sulphate** solution was used as detection method for compound layer

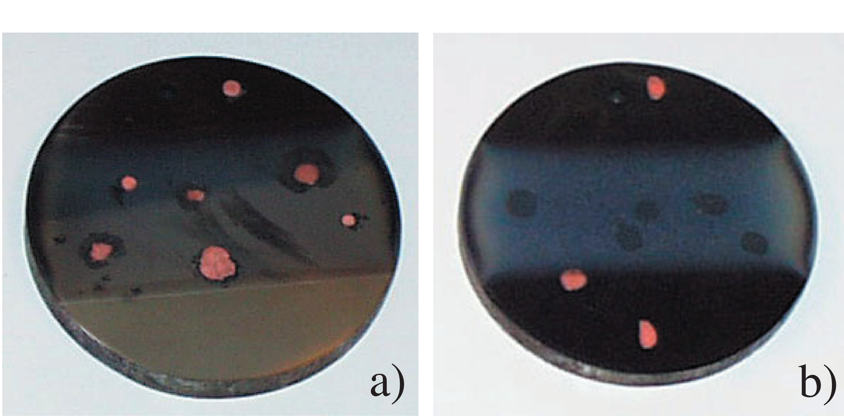


Fig. 4: Redox reaction of copper sulphate solution with treated substrates.
*a) **no compound layer** (just diffusion layer): Cu is reduced whereas Fe is oxidized*
*b) **compound layer** (and diffusion layer): Cu remains dissolved*

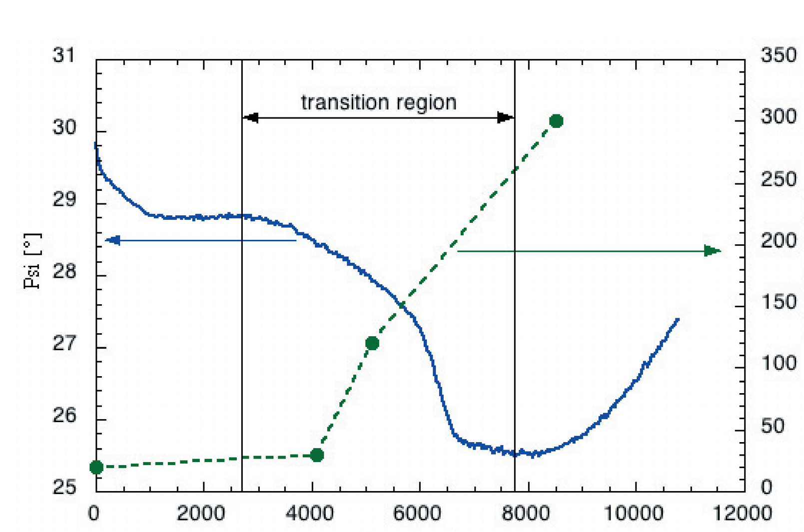


Fig. 7: Relationship between the Ψ signal and the roughness obtained from AFM measurements.

EXPERIMENTAL DETAILS

Fig. 1: The adapted PACVD reactor and the experimental setup of the in-situ ellipsometer.

process pressure	200 Pa
substrate temperature	530°C
discharge voltage	450 V
hydrogen flow (H_2)	102 slh
nitrogen flow (N_2)	50 slh
duration (min)	60-240

Table 1: Process parameters for the nitriding deposition step.
slh .... standard litre per hour

- **XRD (X-ray diffraction)**

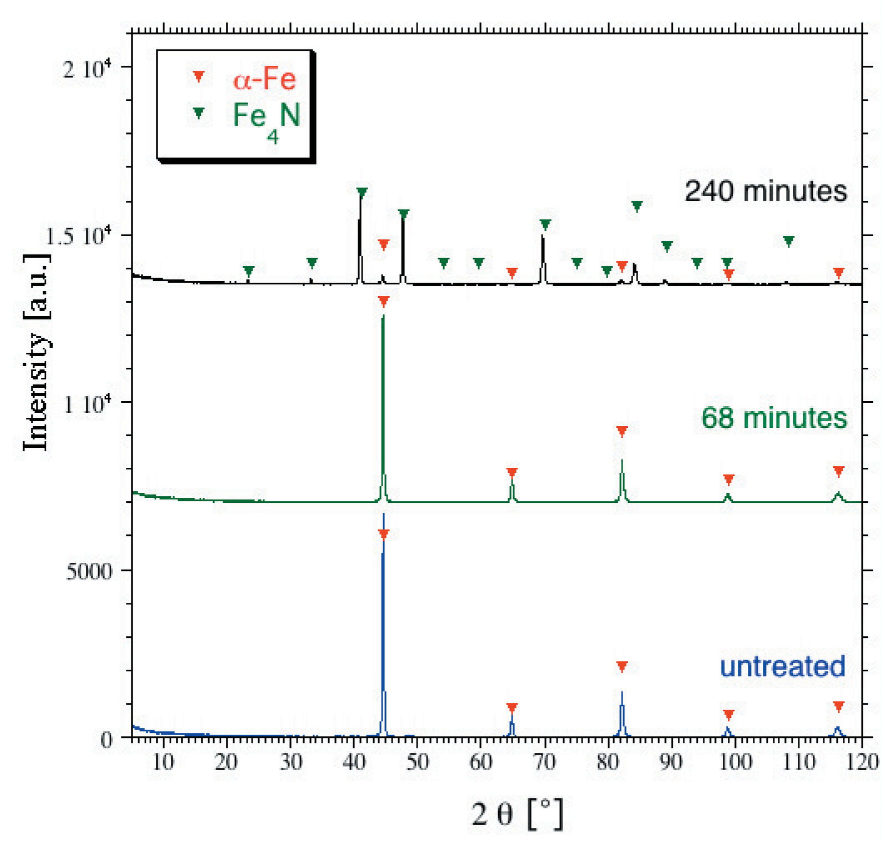


Fig. 7: XRD-patterns of thermochemically treated steel substrates with different nitriding times. bottom: polished substrate; middle: 68 minutes; top: interruption after 240 minutes (compound layer: Fe_4N)

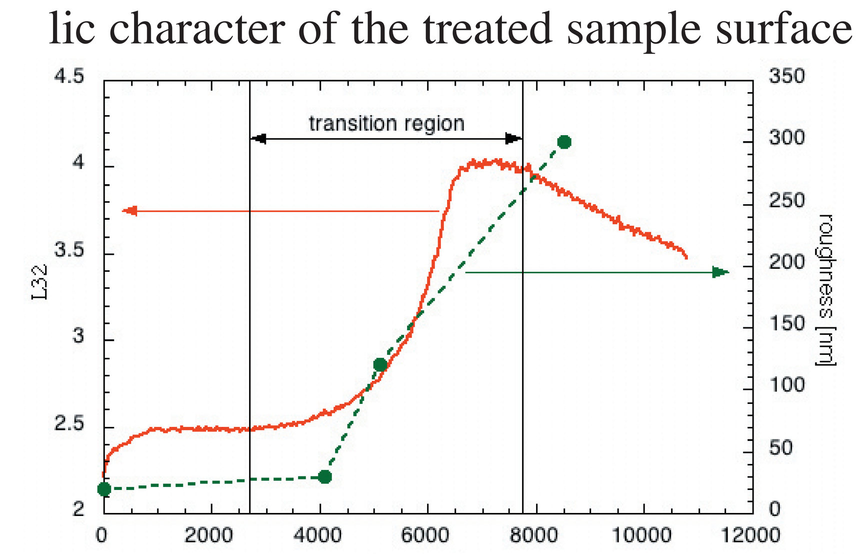
Oscillator model

fit parameter are obtained from the ellipsometric model (Drude-Lorentz model):

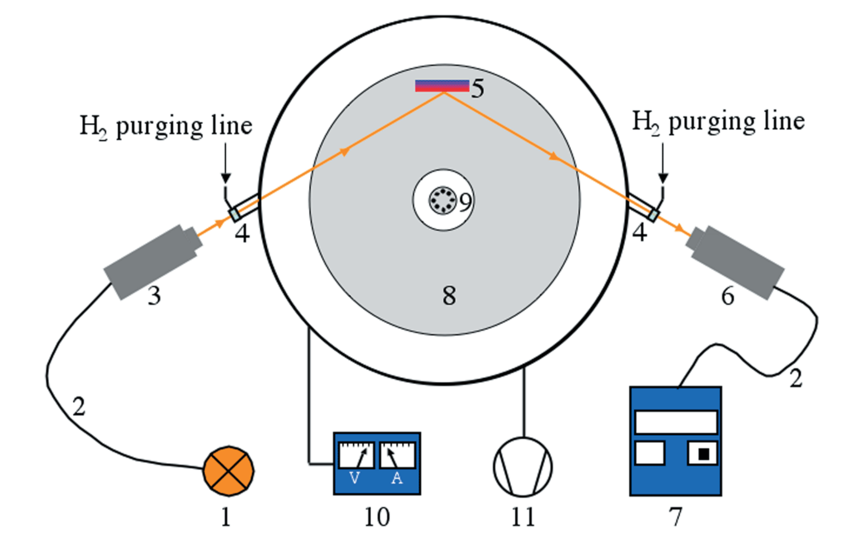
E, L11, L21, L31, L32

E: additive constant of dielectric function
L_{ij}: strength (j=1), position (j=2) broadness (j=3) of the i[th] Lorentzian

- **L32** was taken as **control parameter** to modify the **process variable** (N_2 flow)
- control parameter L32 indicates the metallic character of the treated sample surface



Surface treatment procedures were performed in a hot wall PACVD (plasma-asstisted chemical vapour deposition) reactor (Fig. 1). It is designed for the production of hard coatings as well as for nitriding. To perform on-line measurements of the entire deposition process an *in-situ* spectroscopic ellipsometer (Sentech Instruments GmbH, type SE 801) was used. An schematic view of the experimental setup is shown in Fig. 2. The parameters for the nitriding step are listed in Tab. 1. Mechanically polished steel was used as substrate material.



1: Xe-lamp; 2: optical fibre; 3: emitter; 4: flange & window; 5: sample; 6: detector; 7: control unit; 8: substrate plate; 9: gas shower; 10: pulse generator; 11: pumping unit

Fig. 2: Schematic view of the experimental setup.

Closed loop control (CLC)

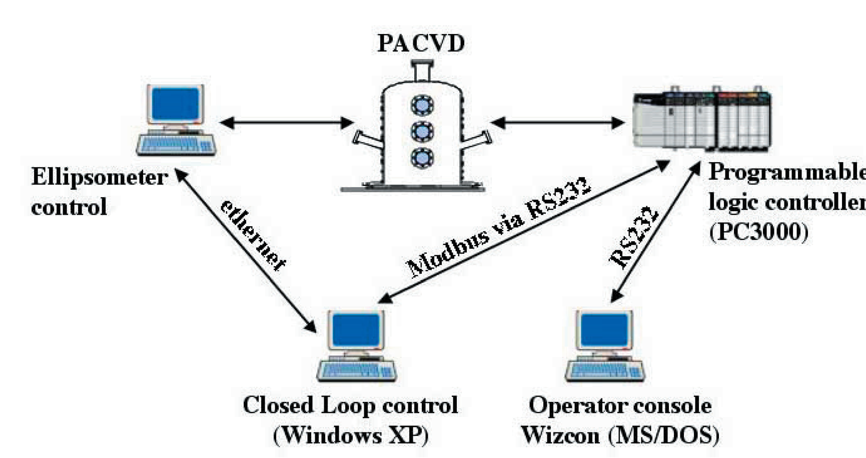


Fig. 9: Computer network of the closed loop control system.

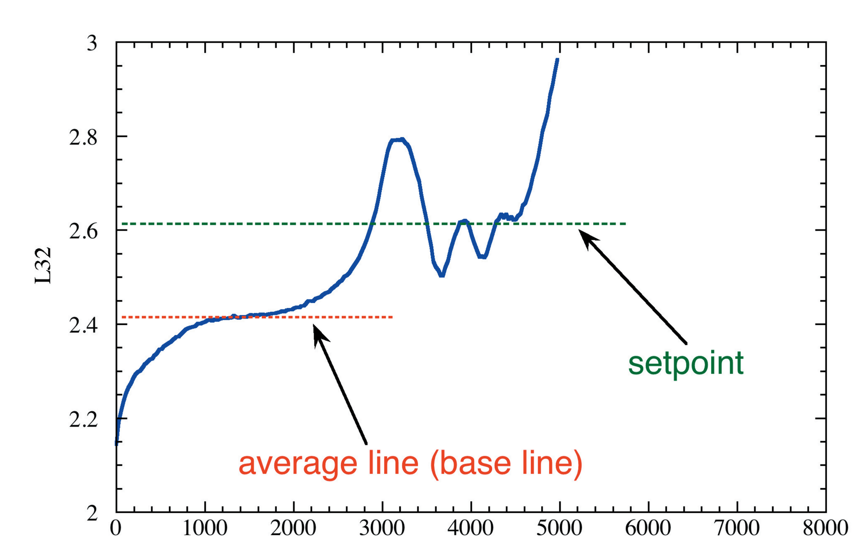


Fig. 10: (Proportional-integral) PI-control of the nitriding step with the average value and the setpoint. The PI-controller starts to regulate the process when the setpoint is passed by the control variable L32 for the first time in order to avoid compound layer formation.

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Fig. 8: Fitting parameter L32 and the resulted drastical roughness increase within the transition region.