

Formation of Nickel-Hydrides in Reactive Plasmas

M. Quaas, H. Ahrens¹, H. Wulff and C.A. Helm¹

Institute of Biochemistry University of Greifswald, F.-Hausdorff-Str. 4, 17487 Greifswald, Germany

¹ Institute of Physics University of Greifswald, F.-Hausdorff-Str. 6, 17487 Greifswald, Germany

The behaviour of hydrogen in metals has attracted scientific attention for many decades and is interesting from both basic research and technological points of view. Metal hydrides find a wide range of applications of which the most prominent is the reversible hydrogen storage. This is of great importance in view of possible future hydrogen economy. Moreover the high diffusivity of hydrogen also makes nanoscaled Me-H systems interesting possibilities for sensor applications, and surface reactions with hydrogen on Pt, Pd, Ni, and other metals are applied in catalysis, particularly in fuel cells.

Most binary metal hydrides are synthesized by solid gas reactions between metal and hydrogen. While some metals easily take up hydrogen (Pd), other form hydrides only under high hydrogen pressure up to 10^9 Pa (Ni) [1, 2, 3].

We have studied in an Ar-H₂ microwave plasma how energy influx influences the metal hydride formation in thin metallic nickel layers (20 nm), i.e. synthesis, phase transformation and reaction rate. The plasma power was kept constant at 700 W, the working pressure was 40 Pa and the substrate (film) temperature during plasma exposure did not exceed 250°C. Only the substrate bias was varied in steps of 25 V from 0 V to -100 V.

In our X-ray experiments at home (combined x-ray reflectometry and high asymmetric Bragg geometry) only a small Ewald reflection sphere could be realized, that means only two or three reflections of the as deposited films and the formed metal hydrides could be observed. To obtain confirmation of the predicted hydride phases grazing incidence measurements at HASYLAB beamline D4 ($\lambda = 0.6882$ Å) at DESY were performed using in-plane geometry. The measured Q-values range from 1 to 12 Å⁻¹.

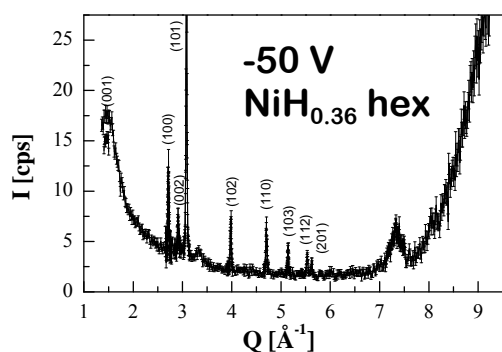


Figure 1: phase composition of Ni films after 10 min plasma treatment, bias voltage -50 V

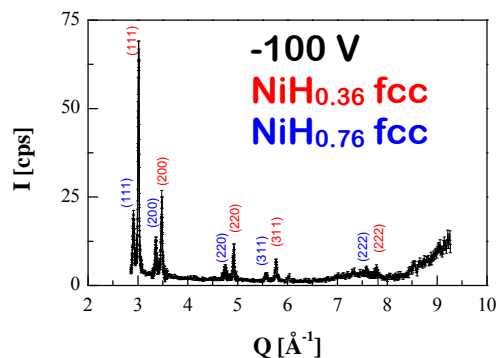


Figure 1: phase composition of Ni films after 500 min plasma treatment, bias voltage -100 V

The evaluation of the diffraction pattern shows that the formation of Ni hydrides in Ar/H₂ plasma depends on bias voltage (Fig. 1, 2) and time of plasma exposure (Fig. 3). Three Ni hydride phases were observed, hexagonal NiH_{0.36} forms in a first quick reaction, fcc NiH_{0.76} and fcc NiH_{0.36} develops as an after-product (Fig. 3) [4,5]. Cubic as well as hexagonal NiH_{0.36} never have been described before to the best of our knowledge. The macroscopic kinetics of these processes is complex as it includes information about simultaneously occurring multiple steps as demonstrated in the chemical equations (Fig. 4). In contrast to high pressure reactions of hydrogen with metallic Ni under plasma exposure we do not observe solid solutions over a wide range of hydrogen concentration [4,5].

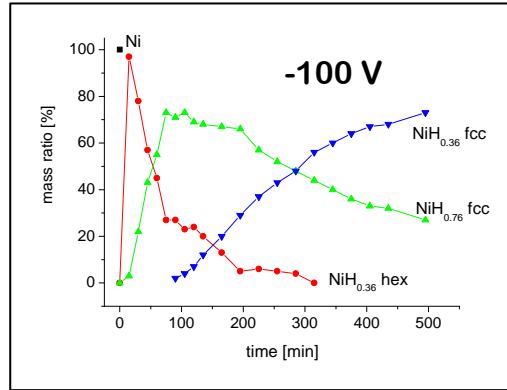


Figure 3: composition of Nickel hydride films after different times of Ar/H₂ plasma treatment.

These plasma chemical experiments show a rather elegant and easy way to produce stable nickel hydride layers under soft plasma conditions. Stoichiometric nickel hydrides were formed under Ar/H₂ plasma exposure in a microwave plasma at low pressure of 40 Pa and substrate temperatures of 200-250°C using different bias voltages (0 V to -100 V). This is quite remarkable because by solid gas reactions nickel hydride can only be formed at high hydrogen pressures at temperatures of 250°C.

These phases are stable at normal pressure and temperatures up to 300°C - 500°C depending on the crystal structure and the hydrogen content. We are convinced, that solid plasma chemistry offers new perspectives both for basic and applied science, especially for metal hydrides.

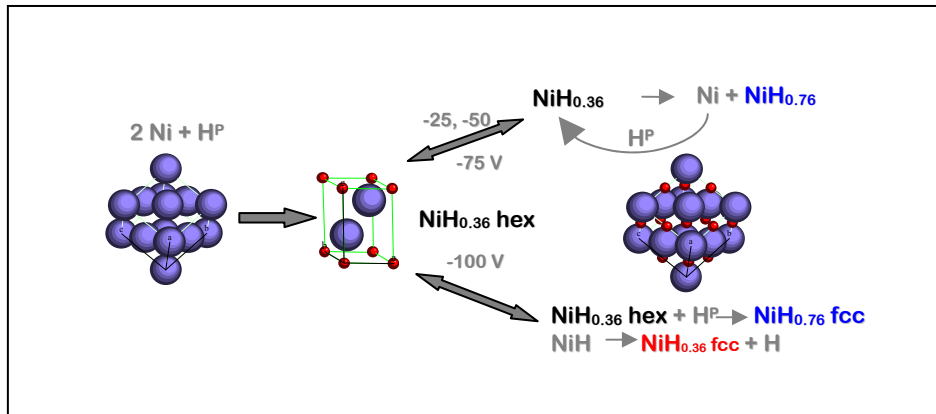


Figure 4: schematic diagram of phase formation and transformation of nickel hydrides under Ar/H₂ plasma exposure.

References

- [1] B. Baranowski, and S.M. Filipek, J. Alloys Comp. **404**, 2 (2005).
- [2] V.E. Antonov, J. Alloys Comp. **330**, 110 (2002).
- [3] V. Azambuja, S. Miraglia, D. Fruchart, S. Tavares, D. dos Santos, and M. Mezour, J. Alloys Comp. **404**, 77 (2005).
- [4] M. Quaas, H. Wulff, O. Ivanova, and C.A. Helm, Surf. Interface Anal. **40**, 552 (2008).
- [5] M. Quaas, H. Wulff, O. Ivanova, and C.A. Helm, Z. Kristallogr., in print.