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Formation of nickel hydrides in reactive plasmas

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Abstract. 20 nm thick nickel films were exposed to argon–hydrogen microwave plasma using different negative bias voltages to study the hydride formation. The formed nickel hydride films were investigated by grazing incidence X-ray diffractometry (GIXD) to control the phase formation. Thickness and density were determined by X-ray reflectometry (XR). The effect of hydrogen plasma depends on the applied negative bias voltage. Without external bias voltage no chemical reaction occurs. At negative substrate voltages (-10 V,-25 V, -50 V, -75 V) a hexagonal Ni_2H phase is formed in a first quick reaction step. In subsequent plasma chemical reactions this Ni_2H is transformed into cubic NiH. The reaction rate of the NiH formation increases with increasing negative bias voltage. The kinetic processes are discussed using a modified isoconversional kinetic analysis which confirms competitive reactions during the NiH formation.

Introduction

Since many years various metal-hydride systems have been studied. 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 in which hydrogen would replace fossil fuels as an energy carrier. Most binary metal hydrides are synthesized by a solid gas reaction between the metal and hydrogen. While some metals and intermetallic compounds easily take up hydrogen, other form hydrides only under high hydrogen pressure up to 10^9 Pa. Nickel forms hydrides only under high hydrogen pressure (> 0.5 GPa) [1,2]. The p-T phase diagram of Ni-H in temperatures up to 630 K and pressures up to 1.8 GPa of gaseous hydrogen was given by Ponyatovskiis group [1]. With rising temperature the difference between the formation and decomposition pressure decreases and disappears at T = 540 K. The decomposition pressure at room temperature is ≤ 0.3 GPa. The nickel hydrides formed at high pressures were shown to have close-packed metal sublattices with f.c.c. structures, in which hydrogen occupies octahedral interstitial positions. Irodova et al. [3] confirmed the existence of NiH_x with $x = 1.05$ and $a_o = 3.740$ Å by neutron diffraction at T = 120 K. Oesterreicher et al. [4] describe high pressure formed nickel hydrides NiH_x with $x =$

0.6 to *x = 0.7* and Zhebelev et al. [5] the f.c.c. structure of $NiD_{0.75}$ (a_o = 3.720 Å) synthesized at high pressure. Khodyrev et al. [6] reported on structure and composition of a hexagonal nickel hydride phase formed when Ni is sputtered in hydrogen. Hemenger and Weik [7,8] have fabricated hexagonal metallic nickel films. The hexagonal lattice parameters reported there are a_0 = 2.622 Å, and c_0 = 4.320 Å. Ni is listed as crystallising in the h.c.p. modification (SG 194). The density was calculated to 7.58 $g{\cdot}cm^{-3}$. The growth conditions are extremely critical for the formation of the h.c.p. structure, which was found to be unstable at room temperature.

A specific challenge in plasma science is the investigation of chemical reactions in solid surface layers as a response to external plasma parameters.

In the focus of this paper are compounds produced from metallic nickel and hydrogen during and after argon-hydrogen plasma exposure using different negative bias voltage. It is difficult to directly modify the behaviour of the neutral particles, but charged particles can be controlled by changing the local electric field, and this is the basis of the bias method. Negative substrate bias accelerates positive ions (Ar^+, Ar_2^+, Ar^{2+}, ArH^+) towards the Ni films. The flux and energy of all positive charged particles bombarding the nickel substrate is modified in steps of - 25 V.

The plasma included reactions were investigated using grazing incidence X-ray diffraction (highly asymmetric Bragg case) and X-ray reflectometry.

Experimental

Thin pure Ni coatings (20 nm) were deposited on Si substrates with 800 nm SiO_2 and 1 nm Cr buffer layers. These films were treated in a microwave plasma source with 10 sccm Ar/ 10 sccm H_2 gas flow without substrate heating. Plasma power and gas pressure were kept constant at 700 W and 50 Pa, respectively. The substrate bias was varied in steps of 25 V from 0 V to -100 V. Within 15 minutes the energy influx by the Ar/H_2 plasma implements a substrate temperature of about 450 K, independent of the used substrate voltage. The samples were characterised during and after plasma exposure by GIXD (asymmetric Bragg case, incidence angle ω= 0.5 °) regarding position, profile and intensities of observed Bragg angles and XR regarding thickness, density and roughness. Both GIXD and XR were performed on a Siemens D 5000 diffractometer equipped with a special reflectometry sample stage for the reflectometry measurements and a special parallel beam attachment (parallel plate collimator) for diffractometry investigations. Cu K_α radiation (40 kV, 40 mA) was used.

Results and discussion

Table 1 gives an overview on the formed nickel hydride phases during argon-hydrogen plasma exposure. Plasma treatment without substrate voltage does not form a new phase, but a clear shift in the peak positions of the Ni reflections to smaller angles can be observed as well an increase of the peak maximum intensity accompanied by a smaller FWHM. The peak shift can be associated with lattice strain induced by external plasma forces which could be explained by the insertion of a small amount of hydrogen. Antonov [1] reports on the existence of NiH_x with x = 0.01 at room temperature up to a hydrogen pressure of 0.4 GPa. At higher pressure an abrupt increase in hydrogen solubility from x = 0.01 to x ≈ 1 is observed. The observed shifts are remarkably different compared to the Ni reflections shift in an argonoxygen plasma. Ar/O_2 plasma causes besides the formation of NiO a shrinking of the Ni unit cell which can be explained by the formation of vacancies activated by ion bombardment [9].

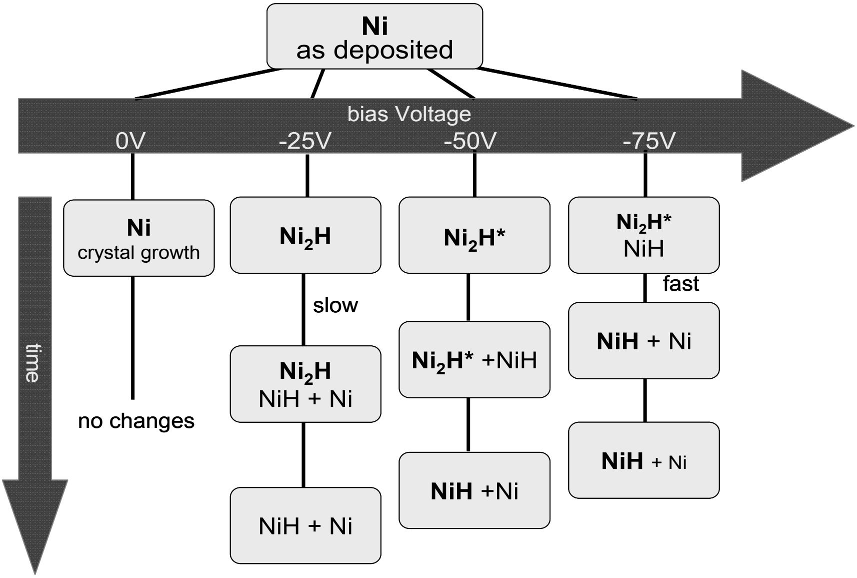


Figure 1. Results of hydrogen plasma treatment.

Ar/H_2-plasma treatment with applied negative bias voltage changes the metallic nickel films into a hexagonal Ni_2H_x phase. Figure 2 shows part of the X-ray patterns of films treated at different bias voltages. Independent of the used bias voltage the phase transformation takes place during the first 15 minutes of plasma exposure. Increasing bias (-10 V to -50 V) decreases drastically the intensity of the Ni_2H_x 002 reflections. The X-ray pattern of the -25 V sample corresponds to the crystal structure of Ni_2H described by Khodyrev et al. [6].The calculated density is 7.45 $g\cdot cm^{-3}$. However, XR measurements of the plasma treated hexagonal Ni_2H_x phase results in densities of about 8.2 $g\cdot cm^{-3}$ and 8.91 $g\cdot cm^{-3}$ for the as deposited nickel films (identically with the density of bulk nickel). The film thicknesses grow about 20 % independent on the bias voltage. The volume of unit cells keeps constant in the margin of error at about 26.2 $Å^3$. The measured density of the plasma treated nickel hydrides is significantly higher than the calculated value for Ni_2H [6] and the calculated density of h.c.p. nickel [7,8]. The measured density of the h.c.p. Ni_2H_x can be explained using the following assumptions. The f.c.c. Ni (a_0 = 3.524 Å) is transformed into in a triple hexagonal cell. The atomic positions change to

Ni (1)	0	0	0	SOF = 1
Ni (2)	1/3	2/3	1/3	SOF = 1
Ni (3)	2/3	1/3	2/3	SOF = 1

with Z = 3, a_0 = 2.411 Å, c_0 = 6.103 Å and V_{UC} = 32.817 $Å^3$. This is in agreement with the space group *P3m1* (No. 156) (Wyckoff 1a, 1b, 1c). Replacing 80 % of the Ni (1) position by

H atoms, the density decreases to 8.2 g·cm^{-3}. The Ni replacement by H in Ni (1) is in accordance with the measured X-ray patterns. The detected lattice constants are a_0 = 2.656(3) Å and c_0 =4.30(2) Å. The clearly smaller c-axis is caused by the replacement/substitution of the Ni-atoms by the smaller H-atoms.

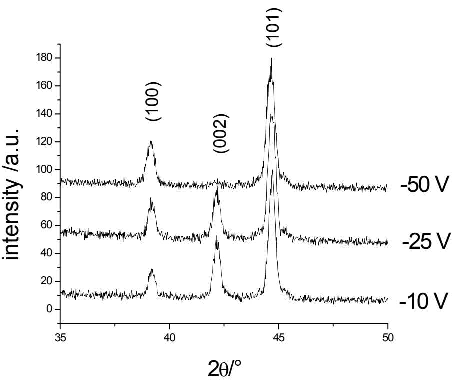


Figure 2a. X-ray pattern of Ni_2H after 15 minutes plasma exposure at different substrate voltages.

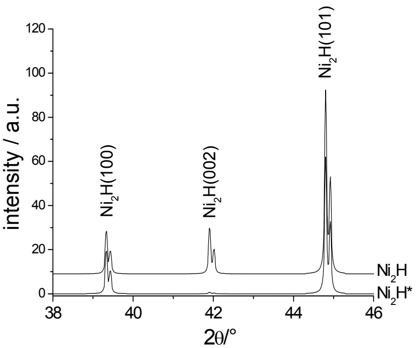


Figure 2b. Simulated X-ray pattern
(1) Ni(2) z=0.25, Ni(3) z=0.75
(2) Ni(2) z=0.4, Ni(3) z=0.68.

From the density measurements we can draw the conclusion that the formed nickel hydride should be described by the formula $Ni_{2.2}H_{0.8}$ (Z=3) or $NiH_{0.36}$. Taking into account this chemical composition and the experimental measured density we can calculate the molecular volume V_{NiH} for $NiH_{0.36}$. The ratio V_{NiH} / V_{Ni} = 1.20 with V_{Ni} the molecular volume of pure metallic nickel. This is in excellent agreement with the measured increase of the film thickness.

The ion impact and the resulting collision cascades cause an amount of structural reordering in the Ni films. Negative bias induces an increasing separation of the hydrogen planes (Ni (1) in the model) from the atomic nickel layers Ni (2) and Ni (3). The Ni layers close ranks in z from 0.25 and 0.75 to 0.4 and 0.68, respectively. By shifting of the z-positions of H,Ni (1), Ni (2) and Ni (3) we can simulate the X-ray pattern as observed in the experiments (figures 2a, 2b). The hexagonal nickel hydride phases characterised by the disappearance of the 002 reflection are labelled Ni_2H^*. Bias voltage -75 V produces directly (that is in the first ten minutes) a new nickel hydride, the f.c.c. NiH_x with a lattice constant of a_0 = 3.725 Å.

X-ray patterns show that continued plasma exposure changes the phase composition in the nickel films. At each operating bias voltage we find a decomposition of the hexagonal Ni_2H_x phase, but the decomposition rate is strongly influenced by the bias voltage (figure 3a). Vice versa the NiH formation increases with increasing negative bias voltage. Up to -75 V the decomposition products are f.c.c. NiH besides metallic f.c.c. Ni. Figure 3b shows the decomposition and formation of the nickel hydride phases at -75 V bias voltages. The unit cell volume of the f.c.c NiH phase is higher than that of pure Ni. For metals of group VIII, the hydrogen volume is practically incompressible and is about 2.7 Å^3 [10]. Taking this into account, the composition of the f.c.c nickel hydride can be specified from the unit cell volumes as $NiH_{0.73}$. This value corresponds to the high pressure phases described in [4].

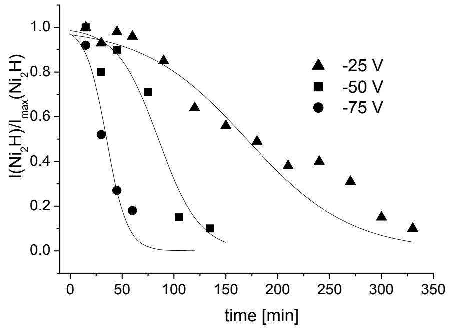


Figure 3a. Decomposition rate of Ni_2H (defined as the normalized integral intensity of Ni_2H 100 reflection) at different bias voltages.

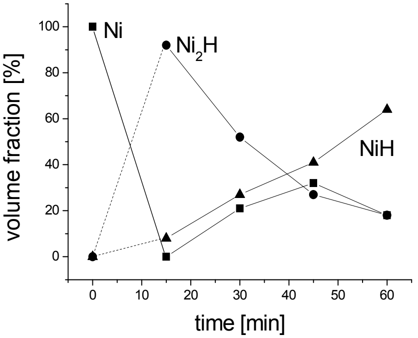
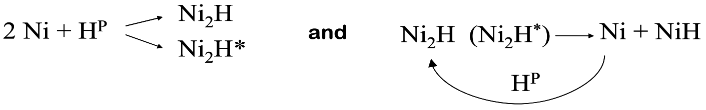


Figure 3b. Change in phase composition during plasma exposure at bias voltage of -75V.

The macroscopic kinetics of these processes shown in figure 3b is complex as it includes information about simultaneously occurring multiple steps as demonstrated in the following chemical equations:



Isoconversional methods [11] allow complex (i.e. multi step) processes to be detected via a variation of the activation energy E_A with α (extend of conversion). Conversely, independence of E_A on α is a sign of a single-step process. From the diffractometry measurements α can be calculated from the integral intensity of Ni_2H_x reflection at the time t divided by the maximum Ni_2H_x intensity (see also figure 3a). In the classical isoconversional analysis α is measured time dependent at different temperatures T and E_A is determined with respect to equation (1)

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_{A,\alpha}}{RT_i} \xrightarrow{\qquad} -\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_{A,\alpha}}{RT_i} \qquad (1)$$

In plasma chemical processes bias voltages U_{bias} influence the energy flux to the substrate. Hence we can take bias voltage analogue to the temperature in the classical isoconversional theory. Therefore, the slope from ln(t) vs.U_{bias} with t the time necessary to reach a certain value of α corresponds to a "plasma activation energy" $E_A^{(plasma)}$. As shown in figure 4 the activation energy depends on the conversion rate that means the kinetics of the $NiH_{0.73}$ formation results from a competition reaction.

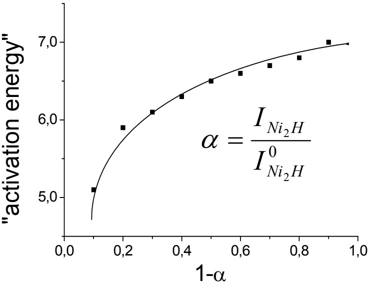


Figure 4. "Activation energy"of the degradation of Ni_2H, caused by different bias voltages.

Conclusions

Two different nickel hydride compounds were formed under Ar/H_2 plasma exposure at low pressure of 50 Pa and temperatures of 500 K using different bias voltages. These phases are stable at normal pressure and temperatures up to 750 K. The hydrogen incorporation takes place discontinuously. h.c.p. nickel hydride ($NiH_{0.38}$) is formed in a first quick reaction step. The kinetics of the f.c.c. $NiH_{0.73}$ formation results from a competition reaction.

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