Piezoresistive Ni:a-C:H thin films
containing hcp-Ni or Ni₃C
investigated by EXAFS and wavelet analysis

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Abstract

Ni:a-C:H thin films obtained by reactive sputtering processes were investigated using EXAFS and subsequent wavelet analysis. Depending on overall thin film deposition conditions, the clusters of Ni in Ni:a-C:H can appear as fcc-Ni or as a non fcc-Ni phase, such as hcp-Ni or Ni₃C. While hcp-Ni and Ni₃C are practically indistinguishable by XRD, the EXAFS analysis can reveal if carbon is the nearest neighbour of Ni or not, thus if Ni₃C is present or hcp-Ni. During our analysis we found, that a wavelet analysis of the EXAFS data is necessary in order to discriminate between hcp-Ni and Ni₃C. Furthermore, we are confident to have identified Ni₃C in our thin films, however, we can not exclude the possibility of the co-existence of hcp-Ni. The results of

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the data evaluation show a good accordance with literature values. Finally, calculations of XRD peaks of hcp-Ni and Ni₃C showed that a discrimination of these two crystal phases might be possible by increasing the cluster size beyond 40 nm.

Keywords: Ni:a-C:H thin film, hcp-Ni, Ni₃C, EXAFS, wavelet analysis

1. Introduction

Metal containing carbon thin films are of great interest due to their unique piezoresistive properties [1–3]. In particular, Ni containing carbon thin films obtained by reactive sputtering processes have proven their potential in piezoresistive applications. Compared to state-of-the-art NiCr functional layers used for steel membrane pressure sensors, Ni-C thin films provide a ten fold higher sensor output signal, while simultaneously their temperature coefficient of resistance can be adjusted to zero for the chosen substrate [3, 4].

The morphology of Ni containing carbon thin films has been studied in terms of transmission electron microscopy and X-ray diffraction (XRD) analysis in a large number of publications [3–7]. It has been shown that the thin films are composed of dense Ni-clusters or Ni-columns which are surrounded by a carbon phase. Depending on the temperature conditions during deposition, the Nickel can appear in its fcc phase or either as a hcp-Ni or a Ni₃C phase [3, 6]. The fcc-Ni is clearly distinguishable from the latter phases by XRD, while the hcp-Ni and Ni₃C are practically indistinguishable in XRD [8].

The origin of the piezoresistive effect of Ni-C composite thin films is still under discussion [3, 9]. For a conclusive transport theory it is helpful to

identify the Nickel phase with certainty. Several papers have been published concerning the nature of the non-fcc Ni phase [10, 11], where samples have been investigated using extended X-ray absorption fine structure analysis (EXAFS) [12]. The samples have been prepared either by pulsed ion beam sputtering [10] or by DC magnetron sputtering [11], whereby the non-fcc phase has been identified as Ni_3C in the EXAFS analysis.

In this paper, we investigate the nature of the non-fcc Ni phase of Ni:a-C:H thin films produced by means of reactive sputtering processes. EXAFS experiments in combination with a wavelet analysis are conducted in order to identify either an hcp-Ni or a Ni_3C phase [13]. In addition, XRD analysis of thin film samples and calculations of XRD based on the results of the EXAFS analysis complete our investigations.

2. Calculations

2.1. XRD

2.1.1. Comparison of calculated hcp-Ni and Ni_3C diffraction data

The distinction between hcp-Ni and Ni_3C phases by XRD is very difficult, because the diffraction peaks of the respective crystal lattice planes are very close [8]. He [8] summarized the XRD peaks up to $2\Theta = 78^\circ$ (Cu- K_α source), where a maximum difference of 0.78° occurs between the hcp-Ni (JCPDS #00-045-1027) and rhombohedral Ni_3C (JCPDS #01-072-1467) at the peak position around $2\Theta = 71^\circ$. Further analysis of these data (see JCPDS data base) for peaks at $2\Theta > 80^\circ$ reveals that there might be more peaks to differentiate between hcp-Ni and rhomb- Ni_3C . However, the differences in the relevant peak positions of the two data sets does not exceed 1° and

respective peaks appear beyond $2\Theta = 125^\circ$, as presented in table 1.

[Table 1 about here.]

Furthermore, Ni_3C generates extra peaks, which are not found in the hcp-Ni diffractogram. Some of these Ni_3C exclusive peaks are summarized in table 2. The signal intensity of those peaks is at least 2 orders of magnitude smaller than the main peak intensity.

[Table 2 about here.]

2.1.2. Peak position, peak broadening, and crystal size effects

If the two phases hcp-Ni and rhomb- Ni_3C are present simultaneously, the peak separation in XRD becomes a challenge, due to peak location, peak intensity, and peak broadening effects. A tentative representation of a hcp-Ni and a rhomb- Ni_3C peak is shown in Fig. 1 ($2\Theta \sim 78^\circ$, crystallite size $D = 15 \text{ nm}$ [3], Cu- K_α). Besides the individual peaks for the two phases, Fig. 1 also shows a sum peak as it would appear in a real XRD experiment in case the two phases are equally distributed and no preference of crystal orientation towards the sample's surface occurs. The noise level is kept to zero in this calculated XRD representation.

In the following, the peak position and peak separation as a function of the wavelength of the X-ray source shall be discussed. The position of a reflection peak in XRD can be described with Bragg's equation

$$\text{const.} = 2d = \frac{n * \lambda}{\sin \Theta}, \quad (1)$$

where d is associated to the crystal plane distance, $n = 1$ is the diffraction order, λ is equal to the wavelength of the X-ray source, and Θ is assigned

to half of the peak position in 2Θ -space. While the plane distance of crystal lattices is constant in case that the crystal is in a thermodynamic equilibrium, the peak position of the XRD signal is only depending on the wavelength of the X-ray source. Thus, using a different X-ray wavelength, peaks should separate clearly in XRD, as seen from eq. (1). However, peak broadening effects according to Scherrer's formula (see eq. (2)) have to be considered as well.

$$\Delta(2\Theta) = \frac{K * \lambda}{D * \cos \Theta} \quad (2)$$

In eq. (2), $K = 1$ is assigned to a shape factor of the crystallites, D is the diameter of the crystallites, and $\Delta(2\Theta)$ is the peak broadening, which is taken as the full width at half maximum (see label b in Fig. 1).

The separation of two neighbouring peaks at $2\Theta_i$ and $2\Theta_{ii}$ can be expressed by the term a as shown in eq. (3).

$$a = 2\Theta_i - 2\Theta_{ii} \quad (3)$$

Using eq. (1), the peak separation of eq. (3) can be calculated for any wavelengths λ_2 , while λ_1 is hold constant at 0.15406 nm (Cu-K $_{\alpha}$).

$$a(\lambda_2) = 2 \left(\arcsin \left[\frac{\lambda_2}{\lambda_1} \cdot \sin \Theta_{i,1} \right] - \arcsin \left[\frac{\lambda_2}{\lambda_1} \cdot \sin \Theta_{ii,1} \right] \right). \quad (4)$$

The peak broadening at the position $2\Theta_{i,2}(\lambda_2)$ and $2\Theta_{ii,2}(\lambda_2)$ is calculated using eq. (2). For simplicity an average value for the peak width of the two individual peaks, assigned as b , was calculated according to eq. (5).

$$\begin{aligned} b(\lambda_2) &= \frac{1}{2} \cdot (\Delta [2\Theta_{i,2}(\lambda_2)] + \Delta [2\Theta_{ii,2}(\lambda_2)]) \\ &= \frac{1}{2} \cdot \frac{\lambda_2}{D} \cdot \left(\frac{1}{\cos \Theta_{i,2}} + \frac{1}{\cos \Theta_{ii,2}} \right). \end{aligned} \quad (5)$$

If a is plotted versus λ_2 an increasing separation of the peak positions with increasing wavelength can be observed. A similar effect can be observed for plotting b as function of λ_2 . Both functions are not displayed here. Instead a more interesting feature is presented in the inset of Fig. 1, where the ratio of a/b versus the wavelength of the X-ray source is plotted. This ratio has an ascent close to zero for increasing wavelengths over a broad range of λ_2 . Eventually, when the argument of the arcsin of eq. (4) and eq. (5) is approaching 1 this ascent is strongly deviating from zero ($2\Theta_2 > 140^\circ$). Finally, the ratio a/b disappears, when the argument of the arcsin is becoming larger than 1 (see inset of Fig. 1 at $\lambda \sim 0.25$ nm).

Because the ratio a/b is nearly constant with respect to λ_2 , a change of the X-ray source will not be helpful for the separation of hcp-Ni and Ni₃C since the sum peak of Fig. 1 will look similar at any given wavelength.

[Figure 1 about here.]

As indicated in the inset of Fig. 1, larger crystallite sizes will increase the a/b ratio and thus the peaks will become distinguishable. Thus, the peak broadening versus the crystallite size was calculated for various peak positions assuming a Cu-K $_{\alpha}$ X-ray source, as presented in Fig. 2. In case the ratio a/b exceeds a value of 2 then the valley of the envelope drops below the FWHM, thus the peaks should be distinguishable (see Fig. 1). Furthermore, it can be seen, that the XRD peaks between 58° and 78° provide a good chance for a peak separation, if the crystallite size can be increased somehow.

[Figure 2 about here.]

2.2. Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS can be used to investigate the nearest neighbourhood of an atom by scanning an energy range around the absorption edge of a specific electron shell of an element and subsequent investigation of the absorption or fluorescence data of the sample [12, 15, 16]. Ni and Ni₃C compounds were subject of a number of studies using EXAFS techniques during the past decade [10, 11, 13]. As presented by Struis et al. [13], we would like to emphasize and expand some aspects of the data analysis concerning Ni₃C and the wavelet analysis (see also Muñoz et al. [16]).

For the analysis presented here we used free available software tools such as the HORAE package (version 071~svn531-1), including ATOMS (version 3.0.1), FEFF6 (version 6.01), ATHENA (0.8.061), and ARTEMIS (0.8.014) under UBUNTU x64-10.04. For the additional wavelet analysis we applied the AGU VALLEN wavelet software (version R2005.1121) [17]. All data plots were generated using the R program package [18].

The crystallographic data of fcc-Ni, hcp-Ni, and Ni₃C were extracted from the JCPDS data base and completed with the Wyckoff parameters (position of the atoms in the unit cell) from the ICSD database, as summarized in table 3.

[Table 3 about here.]

Theoretical $\chi(k)$ data for hcp-Ni and Ni₃C were calculated using ATOMS and FEFF6. The fcc-Ni phase was not considered in this stage, since this phase is clearly distinguishable from the former mentioned phases by XRD. The $\chi(k)$ data resulting from FEFF6 are presented in Fig. 3a. It has to be

noted that the data for hcp-Ni and Ni₃C are very similar. Differences can be spotted in the k -range of 6 to 8 Å⁻¹, however, these might be attributed to signal noise in the evaluation of real data. It has also to be noted that the region below $k = 2$ Å⁻¹ is connected to the XANES (X-ray absorption near edge spectroscopy) region [13], thus, even if there are differences in this region, these can not be considered for further EXAFS evaluations.

The $\chi(k)$ data were further imported into ATHENA for Fourier transformation in order to obtain the $\chi(R)$ data, as presented in Fig. 3b. For this transformation we used a Hanning Window with k in the range of 2 to 20 Å⁻¹, a $dk = 1$, an arbitrary k -weight of 0.5, and with phase correction off. The theoretical $\chi(R)$ of hcp-Ni and Ni₃C appear to be very similar as well. Differences were spotted around the phase-uncorrected distance of $R = 1.2$ Å pertaining to a C-coordination shell in the Ni₃C. Further differences were discovered for $R > 2.75$ Å, although this region might be difficult to evaluate. This region belongs to higher coordination shells, whereas experimental data obtained from samples by EXAFS might be comprised with noise. Thus, the only region available for evaluation is the region mainly before or possibly around the main Ni-Ni shell peak at the phase-uncorrected distance of $R = 2.3$ Å with Fig. 3b.

[Figure 3 about here.]

The carbon signal of the first Ni-C shell at $R = 1.2$ Å (value uncorrected for phase shift) is clearly detected for Ni₃C as seen in Fig. 3b. However, hcp-Ni shows a small shoulder in this region as well. Furthermore, a fit of an hcp-Ni model (first Ni-Ni shell) or an Ni₃C model (first Ni-C and first Ni-Ni

shell) on such a theoretical Ni_3C $\chi(k)$ or $\chi(R)$ data using ARTEMIS produces identical fit parameters for the Ni-Ni shells, thus no distinction seems to be possible by a simple coordination shell fit.

In order to clearly distinguish between these crystal phases, an additional solution to that question was presented by Struis et al. [13], which follows an idea presented by Muñoz et al. [16]. Here, the $\chi(k)$ data and the corresponding $\chi(R)$ data were mapped into one graph, using the so called wavelet analysis. Applying this method, regions in R -space can be connected with k -space regions.

The k -regions that are associated with individual coordination shells can be extracted from FEFF6. The $\chi(k)$ data (backscattering data) of the first coordination shells for the hcp-Ni and Ni_3C are presented in Fig. 4. The first Ni-Ni coordination shell of both, hcp-Ni ($R = 2.62 \text{ \AA}$) and Ni_3C ($R = 2.64 \text{ \AA}$), has its maximum at $k = 6.5 \text{ \AA}^{-1}$, while a small contribution is also visible at $k \sim 2 \text{ \AA}^{-1}$. The Ni-C coordination shell of Ni_3C has its maximum at the same position as the secondary maximum of the Ni-Ni shell ($k \sim 2 \text{ \AA}^{-1}$), however, with a large shoulder ranging to higher k -values.

[Figure 4 about here.]

The peaks of the first two Ni-Ni coordination shells (6 atoms each, $R = 2.62 \text{ \AA}$ and $R = 2.64 \text{ \AA}$, respectively) are dominant in their backscattering amplitudes, in both cases for hcp-Ni and Ni_3C . This makes a wavelet analysis difficult because these signals prevail in a $\chi(k)$ -versus- $\chi(R)$ mapping. Since the EXAFS signal can be understood as a superposition of signals originating from individual coordination shells (see fundamental EXAFS equation in

[12, 16]), single coordination shells may be subtracted from the data.

In particular, the FEFF6-conform structural input file of hcp-Ni and Ni₃C was imported into ARTEMIS and a fit was performed for the first Ni paths. In the fit were included the coordination shells at $R = 2.622 \text{ \AA}$ and $R = 2.638 \text{ \AA}$ for hcp-Ni (each shell filled with 6 atoms) and the shells at $R = 2.629 \text{ \AA}$ and $R = 2.634 \text{ \AA}$ for Ni₃C (filled with 6 atoms each). Since the coordination radii of both shells are very close these shells are treated as one shell filled with 12 atoms in the further analysis.

Later on, the fitted data were exported as $\chi(k)$. The file included the original data, the data for the fit of the coordination shells, as well as the residual data, i.e. original data minus fitted data. These residual data were further evaluated by wavelet analysis using the AGU Vallen Wavelet software. For the wavelet analysis only the data region $k = 2$ to $12 \text{ \AA}^{-1}$ was considered. It has to be noted that k has to be at least larger than $2 \text{ \AA}^{-1}$, otherwise the XANES region will be included which will lead to erroneous signals in the $\chi(R)$ - $\chi(k)$ mapping, due to the presence of other (non-coordination shell-related) features, such as electron transitions [13]. The resulting wavelet data set, as calculated with the AGU-Vallen software, is scaled with k on the x -axis and a frequency value on the y -axis. This frequency can be calculated into phase uncorrected shell distance values in $\text{\AA}$ by multiplying them by $\pi/1000$ [13]. The results of the wavelet analysis on hcp-Ni and on Ni₃C, using calculated $\chi(k)$ data after removing the dominant, first-shell Ni-Ni contribution with each data set, are presented in Fig. 5. The major difference between the respective $\chi(R)$ - $\chi(k)$ plots is found in the region $k = 2 \dots 6 \text{ \AA}^{-1}$ and $R \sim 1.3 \text{ \AA}$. Here, a strong signal appears in the Ni₃C data, which is

missing in the hcp-Ni data. The k -region of this signal corresponds well with the backscattering amplitude of the Ni-C coordination shell as seen in Fig. 4. The R -value is equal to the signal to the left of the Ni-Ni main peak as seen in Fig. 3b. Thus, it is assumed, that this signal is originating from the Ni-C interaction from the first carbon coordination shell.

[Figure 5 about here.]

3. Experimental

3.1. Thin film preparation

Thin films of Ni:a-C:H were obtained by means of a reactive sputtering process. In this deposition process Ni was rf-magnetron sputtered from a Ni target using argon as process gas and C₂H₄ gas as precursor. Prior and directly after the deposition process the samples were heated to 270 °C in the load lock of the sputter equipment. Additional active heating during the sputter deposition was not possible. The sputtering time was kept constant at 10 min for each sample. The atomic ratio of Ni/C of the thin films was adjusted by changing the amount of the precursor gas. Further details of the sputtering process and equipment were described elsewhere [3]. An overview of thin film samples used in EXAFS experiments, including film thickness and atomic percentage of Ni are summarized in table 4.

Silicon pieces (length x width x thickness = 10 mm x 10 mm x 0.55 mm, Si wafer) were chosen as substrates of the thin films for the XRD and EXAFS. The atomic ratio of the thin films was determined by energy dispersive X-ray (EDX) spectroscopy (see table 4) using a scanning electron microscope

JEOL 6460LV equipped with an Oxford Inka 300 spectrometer at an acceleration energy of 6 keV.

A reference Ni_3C sample (powder), which was produced by catalytic reaction and previously characterised by means of EXAFS [13], was kindly provided by PSI (Switzerland). Reference foils of fcc-Ni were kindly provided by the beamline scientists at Bessy II and HASYLAB.

[Table 4 about here.]

3.2. XRD setup

The crystal structure of the Ni phase of the Ni:a-C:H thin films was investigated by grazing incidence X-ray diffraction (GIXRD) with Cu-K_α -radiation ($\lambda = 0.15406$ nm) on a Bruker D8-Focus X-ray diffractometer. The angle of incidence was set to 3.5° . The Ni_3C powder sample was scanned in the $\Theta - 2\Theta$ mode.

The XRD raw data were modified by a background subtraction and a $\text{Cu-K}_{\alpha,2}$ subtraction prior to further evaluation.

3.3. EXAFS setup

EXAFS measurements were performed at Bessy II in Berlin and HASYLAB in Hamburg, Germany. Details of the experimental equipment at the KMC-2 beamline at Bessy II can be found in the literature [19], while corresponding information of the beamline C at HASYLAB are published as well [20]. In both cases the samples were measured in fluorescence mode at room temperature. The Ni absorption edge of the K-line at 8333 eV was

chosen for our investigations. Additional parameters of the measurements are summarized in table 5.

[Table 5 about here.]

3.4. Data evaluation

At first, the data of two scans from each sample were imported into VIPER (V10.18_XD5.36) [21, 22]. The absorption edge was detected at the absolute maximum of the first derivative versus X-ray energy. Further data adjustment procedures are summarized in table 6.

[Table 6 about here.]

After pre-processing the two individual data sets, both were merged in $\chi(k)$ by using the options “sum up currents” and “point-by-point-sum”. The data were checked against the Ni_3C and fcc-Ni model by fitting the first Ni-Ni coordination shell in VIPER (coordination number $CN=12$ in both cases). A test with the hcp-Ni model was not performed because the difference in distance of the first coordination shell of hcp-Ni and Ni_3C is below 1%. The fit of the coordination shell eventually converged towards a shell distance close to the theoretical fcc-Ni or Ni_3C model, respectively. These results of the model fit were compared with the XRD results in order to see if the same crystal phases of Ni were found.

The merged $\chi(k)$ data were exported for further evaluations in ARTEMIS. In ARTEMIS, a fit of the first Ni-Ni coordination shell (coordination number $CN=12$) was performed once more using the appropriate model. The fit was performed in the $\chi(k)$ -space, using a k -weighting of $kw = 0$ and the k range

of 2 to 14 $\text{\AA}^{-1}$. Subsequently, the $\chi(k)$ data of the fit were exported and the residual fit data were extracted for further usage in the wavelet analysis. These data were imported into the AGU Vallen Wavelet software and the wavelet analysis was performed in the range k of 2 to 14 $\text{\AA}^{-1}$.

Finally, the $\chi(k)$ data were fitted with the appropriate model, i.e. for fcc-Ni, hcp-Ni or Ni_3C , in VIPER in order to extract the corrections for E_0 , the coordination shell distances of the first two shells and the Debye-Waller factors. Further details of the fit parameters are listed in table 7.

[Table 7 about here.]

Finally, results from XRD analysis and coordination shell fits from EXAFS data were taken to model a theoretical lattice of the Nickel phase of the samples investigated. The modelling was performed using POWDERCELL [14], where XRD data can be calculated by supplying appropriate crystal structures as input. Further parameters for XRD calculations are listed in table 8.

[Table 8 about here.]

4. Results

4.1. XRD

The measured diffractograms of the Ni:a-C:H thin film samples and the Ni_3C reference sample (PSI, Switzerland) are presented in Fig. 6. The peak positions and relative intensities are summarized in table 9.

The Ni_3C reference sample and the thin film samples containing Ni_3C exhibit a shift of the diffraction peaks towards lower 2Θ values compared to

calculated peak positions. Furthermore, the extra peaks that would clearly distinguish an Ni_3C phase from a hcp-Ni phase (see table 2) could not be detected in the XRD diffractograms.

The fcc-Ni thin film sample shows up differently. First, all peaks are shifted to slightly higher values in 2Θ -space. And, second, a peak at $2\Theta=47.5^\circ$ appeared which might be assigned to a carbon phase (JCPDS #80-0004).

[Figure 6 about here.]

[Table 9 about here.]

4.2. EXAFS

Graphical representations of the EXAFS data, such as $\mu(E)$ in the XANES and the EXAFS region, $\chi(k)$, and $\chi(R)$, are shown in Fig. 7 to Fig. 10, respectively.

The raw data were briefly evaluated using the ATHENA software package. ATHENA chooses the value of E_0 automatically at the maximum of the first derivative with the experimental $\mu(E)$ data.

In general, the samples containing only fcc-Ni can be clearly distinguished from the Ni_3C containing samples because their $\mu(E)$, $\chi(k)$, and $\chi(R)$ graphs exhibit significant differences.

4.2.1. The fcc-Ni samples

The fcc-Ni containing Ni:a-C:H thin film sample and the Ni foil reference exhibit very similar $\mu(E)$ patterns in the XANES and EXAFS region (see Fig. 7 and Fig. 8). The first derivative of the $\mu(E)$ data in the XANES region, as shown in Fig. 7b, reveals several local maxima with the largest

ones around 8333 eV and 8343 eV, respectively. The first maximum is higher compared to the second one for both, the fcc-Ni reference and the fcc-Ni containing Ni:a-C:H thin film, respectively.

The only difference in the EXAFS data can be seen right after the absorption edge, where a small extra maximum appears with the fcc-Ni reference sample (see arrow in Fig. 8). However, this region belongs to XANES and is not further considered in our EXAFS evaluation. The $\chi(k)$ patterns, as presented in Fig. 9, are similar for both samples, although a slight shift in k seems to exist for the local maxima and minima of $\chi(k)$. The $\chi(R)$ data for the fcc-Ni containing samples appear very similar as well (see Fig. 10), although slight differences were spotted in the position of the maxima and minima (R -values). Finally, the shoulder to the left of the main peak at around $R = 2.2$ Å is slightly more pronounced in the thin film sample, compared to the fcc-Ni reference foil.

4.2.2. Samples containing Ni_3C

The $\mu(E)$ patterns of Ni_3C containing samples in XANES and EXAFS are nearly indistinguishable, regardless if we take the reference sample, the Ni:a-C:H thin film sample with pure Ni_3C or with a Ni_3C and a fcc-Ni phase (see Figures 7 and 8). Slight differences arise only at $E=8450$ eV and between 8500 and 8550 eV.

The XANES region reveals several maxima in its first derivative, as also observed for the fcc-Ni samples. However, the maxima with the highest magnitude appear in all three samples around 8343 eV, which is in contrast to the fcc-Ni samples (see Fig. 7b). Finally, no significant difference in $\chi(k)$ or the $\chi(R)$ data could be detected as seen in Fig. 9 and Fig. 10, respectively.

[Figure 7 about here.]

[Figure 8 about here.]

[Figure 9 about here.]

[Figure 10 about here.]

4.3. Wavelet analysis

The results of the wavelet analysis after removal of the dominating Ni-Ni first coordination shell peak are depicted in a series of graphs of Fig. 10. Regarding samples containing a non-fcc Ni-phase, the data appear to be consistent with the wavelet analysis of a theoretical Ni_3C model as presented in Fig. 5b. The Ni_3C reference sample (see Fig. 10e) shows a clear signal at the position $k = 3.9 \text{ \AA}^{-1}$ and $R = 1.32 \text{ \AA}$ (phase uncorrected), which is associated with the first carbon coordination shell around the central Ni atom [13]. A similar signal can be spotted on the data obtained from Ni:a-C:H thin films, which contain a non-fcc Ni phase.

The corresponding results on the fcc-Ni samples, i.e. the reference Ni foil and the fcc-Ni containing Ni:a-C:H thin film, differ significantly from the results obtained with Ni_3C samples. The signal associated with carbon is missing in the wavelet analysis data, as exhibited in Figures 11a and 11b. A weak signal is visible on both data sets in the k range of 2 to $4 \text{ \AA}^{-1}$ and for a $R \sim 1 \text{ \AA}$, however, this feature is likely an artefact from the XANES region, from the Fourier Transformation by using a finite (instead of infinitely large) k interval, or from interference effects resulting from higher order coordination shells of Ni. However, the fcc-Ni related data sets themselves are consistent,

showing similar patterns for the reference Ni foil and the fcc-Ni containing thin film sample.

Table 10 summarizes the results of the wavelet analysis with positions of the dominating Ni peak before and positions of the C peaks after the removal of the first Ni-Ni coordination shell. The position of the Ni peak of the fcc-Ni reference and the thin film sample in k -space with $k \sim 5.9 \text{ \AA}^{-1}$ is close to the calculated value of $6.1 \text{ \AA}^{-1}$, although the R values ($R \sim 2.07 \text{ \AA}$) are somewhat large compared to theory. The Ni peak position in Ni_3C containing samples differs significantly from calculated values, whereby $R \sim 2.04 \text{ \AA}$ (theory $R = 2.17 \text{ \AA}$) and $k \sim 4.7 \text{ \AA}^{-1}$ (theory $k = 5.9 \text{ \AA}^{-1}$) were obtained during analysis. The position of the C peak in Ni_3C samples after removal of the dominating first Ni-Ni shell is close to theoretical values with $R \sim 1.31 \text{ \AA}$ and $k \sim 3.5 \text{ \AA}^{-1}$ (theory: $R = 1.26 \text{ \AA}$ and $k = 3.2 \text{ \AA}^{-1}$).

[Figure 11 about here.]

[Figure 12 about here.]

[Table 10 about here.]

4.4. Coordination shell fits with VIPER

The $\chi(k)$ data of the samples under investigation in this paper were fitted with the VIPER software, using the appropriate crystal structure model according to results of the wavelet analysis. One exception had to be made: the data of the Ni:a-C:H thin film sample containing fcc-Ni and Ni_3C was fitted using the Ni_3C model only. Further fitting parameters used for the analysis

can be found in table 7 in section 3.4. The results of the coordination shell fits are presented in table 11.

The fitted Ni-Ni distance of the fcc-Ni reference and the fcc-Ni containing Ni:a-C:H thin film sample matches well with the theoretical data. It has to be noted that the absorption edge energy shifts to higher values according to the fit in comparison to the theoretical value. In case of the fcc-Ni reference, the new E_0 corresponds roughly with the second maximum in the XANES region as presented in Fig. 7b. As for the fcc-Ni containing thin film, E_0 seems to be at the small shoulder to the left of the second maxima, as exhibited in Fig. 7b. But it has also to be noted that the shift in E_0 and the standard deviation of this fitting parameter have the same magnitude in both cases.

The Ni₃C reference sample as well as the Ni₃C-containing thin film sample, both exhibit similar distances for the Ni-Ni coordination shell fit, which are close to the theoretical value of 2.63 Å. The standard deviation is reasonably low ($\sim 1\%$) for this coordination shell fit. Furthermore, no shift in absorption edge energy has been observed, although E_0 was initially set to 8343 eV. The fit of the carbon shell reveals slight differences compared to reported crystal structure data. First, the standard deviation for the coordination shell distance is rather high ($\sim 10\%$). And, second, the reference sample exhibits a slightly lower coordination shell distance, whereas the thin film sample reveals a slightly higher shell distance compared to simulations using reported crystal structure data.

The Ni:a-C:H thin film sample containing a fcc-Ni and a Ni₃C phase exhibits fitting parameters that are somewhat closer to the theoretical data.

The edge energy E_0 does not shift during the fit. The Ni-Ni shell distance is significantly lower than the one expected for Ni_3C , while the C-Ni distance is slightly higher compared to calculations.

[Table 11 about here.]

4.5. XRD fits

The positions of the measured XRD peaks presented in table 9 show a deviation compared to the peak position of powder samples of the JCPDS data base. In the subsequent analysis we assumed that the experimental error of the XRD measurement is kept to a minimum, thus the peak position shift due to sample positioning errors would be negligible. Therefore, the shift of the peak position is attributed to a deviation of the crystal unit cell size from ideal values.

The theoretical XRD peak positions obtained by crystal unit cell modeling of fcc-Ni and Ni_3C , respectively, using POWDERCELL are presented in table 12. In general, the calculated XRD peaks up to $2\Theta = 80^\circ$ matched well with measured data, while a growing divergence between calculation and measurement was observed beyond that angle.

The distance of the first coordination shell obtained by unit cell modeling of fcc-Ni data matched well with the data obtained in EXAFS analysis (compare tables 12 and 11). Differences were observed for the Ni_3C samples in bond lengths of Ni-Ni and Ni-C of the first coordination shells in the POWDERCELL calculations compared to EXAFS analysis. As for the Ni_3C powder sample, the Ni-Ni coordination shell distance matched well in both analyses. However, the Ni-C distance obtained from unit cell modeling is significant

larger compared to the EXAFS results. Furthermore, the Ni_3C containing thin film sample revealed an opposite behavior: The Ni-C distance obtained by POWDERCELL and EXAFS matched well, however, the Ni-Ni distance showed a significant deviation.

The thin film containing both crystal phases, Ni_3C and fcc-Ni, was excluded for further XRD peak fits. A good match of calculated Ni_3C peaks with the measured data could be established without any change in the size of the unit cell, however, the fcc-Ni peak fit could not be established. The second largest peak of the unmodified fcc-Ni unit cell matched well the calculated and measured XRD peak positions, however, the largest peak exhibited a deviation about 0.5° (measured at 45.014° , calculated at 44.497°). A fit of the largest peak of fcc-Ni could be established by changing the unit cell size, however, the second largest peak could not be fitted any more (measured at 51.894° , calculated at 52.414° by 1% unit cell size increase).

[Table 12 about here.]

5. Discussion

This study focuses on the investigation of Ni:a-C:H thin films by means of XRD and EXAFS in order to clarify if the non fcc-Ni phase found in these thin films is actually hcp-Ni or Ni_3C .

XRD studies alone yield inconclusive results, since the lattice spacings of hcp-Ni and Ni_3C are too similar, as also discussed in the literature [8]. An in depth-analysis of calculated XRD data revealed that Ni_3C generates additional peaks compared to hcp-Ni, although they are at least 2 orders of

magnitude smaller than the largest peak. Thus, sample preparation and XRD measurement become a challenge in order to get sufficiently large signal-to-noise ratio with the diffractograms. If both crystal phases, Ni_3C and hcp-Ni, are present simultaneously in a sample, an increase of crystallite size would be beneficial, because the XRD signals will become narrower and more clearly distinguishable. However, the crystal growth in thin films and in powder samples is strongly connected to the temperature of the preparation process. Thus, if the temperature is increased in order to promote crystal growth, then, the overall thermodynamic conditions might change and Ni_3C or hcp-Ni will directly be transformed to fcc-Ni (transition temperature during thin film deposition between 200 and 400 °C [5], transition temperature of Ni_3C nanoparticles obtained from a solution about 400 °C [23], transition temperature of hcp-Ni about 380 °C [24]).

EXAFS studies were performed to discriminate the hcp-Ni and the Ni_3C phase. It is shown that a fit of $\chi(k)$ or $\chi(R)$ data alone is inconclusive, because both crystal models produce equal fit results and parameters when only lower coordination shells are applied (Ni-C and Ni-Ni for Ni_3C and Ni-Ni for hcp-Ni). Using the method of wavelet analysis a clear distinction between Ni_3C and hcp-Ni becomes possible, because the Ni_3C case develops a clear signal associated with a Ni-C coordination shell, which is not existent in a hcp-Ni structure. Our EXAFS experiments of samples containing a non fcc-Ni phase reveals this Ni-C coordination shell peak in the wavelet analysis. This signal was also detected in data obtained with a Ni_3C reference powder sample [13]. Furthermore, Ni:a-C:H thin film samples with only fcc-Ni did not show that Ni-C signal in wavelet analysis. Thus, we conclude the carbon

matrix surrounding the Ni clusters or columns [3, 6, 7] does not affect the wavelet analysis. Therefore, the signal found in wavelet analysis of the non fcc-Ni sample can be clearly attributed to a Ni_3C phase.

Further analysis of the samples containing both, fcc-Ni and Ni_3C phases reveals a strong signal associated with a Ni-C coordination shell. Due to the strength of the Ni-C signal in these data and the rather small signals of higher Ni-Ni coordination shells, doubts arise at this point for a sole presence of a Ni_3C phase in Ni_3C samples investigated here. It cannot be excluded that Ni_3C and hcp-Ni might coexist in the thin films. A clear distinction might be possible by the methods described above, i.e., the XRD analysis in combination with increasing the grain size of the Ni or Ni-C clusters. Furthermore, an exact analysis of the atomic composition of the Ni-C clusters (or columns, see [6, 7]) would be beneficial in order to be able to identify the crystal phases with certainty.

The coordination shell distance-fits of the EXAFS data give conclusive results between thin film samples, reference samples, and literature values [11, 13]. Subsequent XRD modeling gave inconclusive results. The measured diffraction peaks of the Ni_3C samples matched well with calculated diffraction data by a uniform increase of the unit cells. However, the coordination shell distances of the calculated XRD data and the EXAFS analysis did not match entirely. The observed differences may have several origins. As for the Ni-C in the powder sample, the bond length obtained by EXAFS has a standard deviation of 0.2 Å, thus the bond length obtained by POWDERCELL is in the range of the measurement error. The divergence in the fitting results for the Ni_3C thin film samples may be caused by in-built thin film stress (sput-

tering process). Further reasons for the deviation of XRD fits and EXAFS analysis can be: First, the crystal structure is not exactly that of Ni_3C [25]. This may lead to similar results in the inherently less precise wavelet analysis, as is also applied in this paper. However, the coordination shell distance according to the $\chi(k)$ -fit can reveal slight differences between the distances very sensitively. Second, the samples contain several rather stable phases such as Ni_3C , Ni_2C , and NiC [25]. In this case the same points as presented above will hold. Third, the Ni_3C samples contain both, hcp-Ni and Ni_3C , phases. Thus, the coordination shell distances might be correct, although the XRD measurements were performed with a far too low resolution or size of the crystallites, in order to distinguish between these phases.

6. Conclusion

Thin film samples of Ni:a-C:H were investigated by means of EXAFS in order to identify whether hcp-Ni or Ni_3C is present. It was shown that a wavelet analysis of the EXAFS data is necessary in order to identify a C shell around the Ni. Sole $\chi(k)$ or $\chi(R)$ analysis and model fits do not provide enough evidence to distinguish between hcp-Ni and Ni_3C . A clear 1st order coordination shell of C could be detected around the Ni by wavelet analysis. Thus, we state to have found Ni_3C in our samples.

Sole hcp-Ni was not found in our experiments; however, we cannot exclude the co-existence of an hcp-Ni besides a Ni_3C phase. Since the crystal data of hcp-Ni and Ni_3C are very similar, further studies involving EXAFS and advanced XRD analysis might be necessary in order to clarify if an hcp-Ni phase really exists.

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Figure 1: Peak separation a and peak width b of hcp-Ni (JCPDS #00-045-1027) and Ni_3C (JCPDS #01-072-1467), assuming an $\text{Cu-K}\alpha$ X-ray source ($\lambda = 0.15406$ nm) and a crystallite size of $D = 15$ nm. The inset shows the ratio a/b versus X-ray wavelength.

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(a) Wavelet analysis of hcp-Ni.

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Figure 7: XANES region of reference samples and the thin film samples.

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Figure 9: $\chi(k)$ conversion of the data presented in Fig. 8. The conversion was performed in ATHENA, using $E_0 = 8333$ eV for all pure fcc-Ni samples and $E_0 = 8343$ eV for all samples containing Ni_3C (automatically chosen by ATHENA). The shaded area below $k = 2 \text{ \AA}^{-1}$ belongs to the XANES region.

Figure 10: $\chi(R)$ conversion of EXAFS data from Fig. 8. For the $\chi(k)$ to $\chi(R)$ Fourier Transformation in ATHENA were used a Hanning Window with k in the range of 2 to 12 $\text{\AA}^{-1}$, a $dk = 1$, an arbitrary k -weight of 0.5, and with the phase correction switched off.

(a) fcc-Ni, reference foil, sample #3.

(b) fcc-Ni, Ni:a-C-H thin film sample (#1).

(c) Ni_3C and fcc-Ni containing Ni:a-C:H thin film sample (#8).

(d) Ni_3C , Ni:a-C:H thin film sample (#17).

(e) Ni_3C , reference sample from PSI (#4).

Figure 10: Wavelet analysis of residual $\chi(k)$ data after the removal of the Ni-Ni coordination shell data from the EXAFS data set. The strong signal for the k range of 2 to 4 $\text{\AA}^{-1}$ and at $R \sim 1.2 \text{\AA}$ is associated with a carbon coordination shell surrounding Ni (see 10c, 10d, 10e).

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<u>rhomb-Ni₃C</u>			<u>hcp-Ni</u>			Separation in $^\circ$
(h k l)	2Θ in $^\circ$	Intensity	(h k l)	2Θ in $^\circ$	Intensity	
(4 1 0)	127.079	0.029	(2 1 0)	127.668	0.035	0.589
(1 4 3)	131.828	0.112	(2 1 1)	132.427	0.227	0.599
(4 1 3)	131.828	0.112				
(1 1 15)	145.952	0.152	(1 0 5)	144.999	0.148	-0.953
(4 1 6)	149.188	0.067	(2 1 2)	149.92	0.114	0.732
(1 4 6)	149.188	0.067				

Table 2: Selection of calculated XRD peaks (using POWDERCELL [14]), which appear in the diffractogram of Ni_3C (JCPDS #01-072-1467) and not in hcp-Ni (JCPDS #00-045-1027). The intensities are normalized to a value of 1 in respect to the main peak.

(h k l)	2Θ in $^\circ$	Intensity
(0 1 2)	26.462	0.011
(1 0 4)	35.912	0.004
(2 0 2)	48.222	0.001

Table 3: Crystallographic data of fcc-Ni (JCPDS #00-004-0850), hcp-Ni (JCPDS #00-045-1027, ICSD #76668), and Ni₃C (JCPDS #01-072-1467, ICSD #17005).

	fcc-Ni	hcp-Ni	Ni ₃ C
space group	Fm-3m	P6 ₃ /mmc	R-3c
crystallographic axis (a, b, c) in 1 Å	3.5238, 3.5238, 3.5238	2.622, 2.622, 4.321	4.553, 4.553, 12.920
crystallographic angles (α, β, γ) in °	90, 90, 90	90, 90, 120	90, 90, 120
Wyckoff-Parameter: Element	Ni $< 0, 0, 0 >$	Ni $1/3, 2/3, 1/4 >$	$< \text{C} < 0, 0, 0 >$ Ni $< 1/3, 0, 1/4 >$
$< x, y, z >$			

Table 4: Overview of samples examined in EXAFS experiments including selected properties of the Ni:a-C:H thin films.

Sample #	Film thick- ness in nm	amount of Ni in at%	Crystal phase ac- cording to XRD
1	282	55	fcc-Ni
3 ^a	-	100	fcc-Ni
4 ^b	-	-	Ni ₃ C
8	347	62	(hcp-Ni or Ni ₃ C) + fcc-Ni
17	409	59	hcp-Ni or Ni ₃ C

a Reference foil at Bessy II

b Reference sample from PSI

Table 5: Experimental setup and scan parameters of the EXAFS measurements.

	Bessy II, KMC-2	HASYLAB, Beamline C
Equipment details	[19]	[20]
Absorption edge	8333 eV	8333 eV
Measurement mode	Fluorescence	Fluorescence
Sample position	45° to incident beam	35 °, 45°, and 50°, respectively to incident beam
Detector position	90° to incident beam	90° to incident beam
Scanning energy range	8100 eV – 9100 eV	8100 eV – 9100 eV
Start XANES range	8280 eV	8300 eV
Step width below XANES range	1 eV	10 eV
Start EXAFS range	8380 eV	8380 eV
Step width below EXAFS range	1 eV	0.5 eV
Step width in EXAFS range	Steadily increasing from 1 to 5 eV until end of scan	Steadily increasing from 1.2 to 5.5 eV until end of scan

Table 6: Options for EXAFS data pre-processing in VIPER.

Option	Value / Adjustments
Converting	“Use original energy mesh”
Pre-edge range	8100 eV - 8250 eV
Post-edge background fit	(1) “Bayesian-smoothing” (2) “Smoothing spline”
Remaining pre-processing parameters	Default

Table 7: Parameters for EXAFS data fit in VIPER.

	Ni ₃ C model	fcc-Ni model
Coordination shells and coordination numbers (CN)	Ni-C, $CN = 2$ Ni-Ni, $CN=12$	Ni-Ni, $CN=12$
Edge energy for shells	$E_{0,Ni-C} = E_{0,Ni-Ni}$	
k -range for fit in $\text{\AA}^{-1}$	2...14	2...14
k -weight of $\chi(k)$ for fit	1	2

Table 8: Parameters used for XRD calculations in POWDERCELL.

X-ray source	Cu-K $_{\alpha,1}$
Geometry	Debye-Scherrer
Full-width half maximum	7
Background value	0

Table 9: Peak positions of XRD analysis with relative peak intensities as obtained by the EVA software (version 12.0.0.0, 2006).

Peak	fcc-Ni (thinfilm)		Ni ₃ C/fcc-Ni (thinfilm)		Ni ₃ C (thinfilm)		Ni ₃ C (PSI)	
	Position	Intensity	Position	Intensity	Position	Intensity	Position	Intensity
	2 Θ in $^{\circ}$	in %	2 Θ in $^{\circ}$	in %	2 Θ in $^{\circ}$	in %	2 Θ in $^{\circ}$	in %
#1	44.658	100	39.608	18.7	39.442	21.0	39.121	18.4
#2	52.004	19.3	41.938	12.1	41.808	16.7	41.484	23.5
#3	76.601	13.6	45.014	100	44.862	100	44.536	100.0
#4	93.130	11.7	51.894	1.3	58.768	11.4	58.4	14.6
#5			58.933	11.6	71.458	9.1	71.05	11.3
#6			71.634	9.2	78.384	8.4	77.952	11.4
#7			78.533	8.0	86.304	7.0	85.842	10.0
#8			86.539	5.0	88.450	5.2	87.936	6.8
#9			88.587	3.5	98.801	2.9		

Table 10: Results of wavelet analysis.

Sample	Crystal phase	Crystal phase	E_0 in eV	1st Ni-shell — original data		C-shell — after removal of 1st Ni shell	
	XRD	EXAFS		k in $\text{\AA}^{-1}$	R_{uncorr} in $\text{\AA}$	k in $\text{\AA}^{-1}$	R_{uncorr} in $\text{\AA}$
fcc-Ni	theory	theory	8333	6.2	2.01		
#3		fcc-Ni	8332.7	5.8	2.10		
#1	fcc-Ni	fcc-Ni	8333.2	5.9	2.04		
#8	fcc-Ni/Ni ₃ C mixed	Ni ₃ C	8343.1	4.8	2.01	3.2	1.29
#17	Ni ₃ C	Ni ₃ C	8343.6	4.7	2.01	3.3	1.32
#4		Ni ₃ C	8342.5	4.5	2.10	3.9	1.32
Ni ₃ C	theory	theory	8333	5.9	2.17	3.2	1.26

Table 11: Fit of coordination shell distances according to VIPER. The coordination shell number of the C-shell was set to 2, the number of atoms in the Ni-shell was set to 12 for fcc-Ni and Ni₃ containing samples. E_0 – absorption edge energy, ΔE_0 – shift in absorption edge energy (result of data fit), R – coordination shell radius (phase corrected), DW – Debeye-Waller factor.

Sample	Crystal phase		C				Ni		
	XRD	EXAFS	E_0 in eV	ΔE_0 in eV	R in Å	DW	ΔE_0 in eV	R in Å	DW
fcc Ni		Theory	8333.0				0	2.49	
#3		fcc-Ni	8332.7				10.4 ± 9.6	2.50 ± 0.07	0.019 ± 0.005
#1	fcc-Ni	fcc-Ni	8333.2				6.8 ± 6.6	2.49 ± 0.04	0.010 ± 0.003
#8	fcc-Ni	Ni ₃ C	8343.1	-2.5 ± 0	1.97 ± 0.13	0.052 ± 0.051	-2.5 ± 2.6	2.59 ± 0.03	0.018 ± 0.003
		+							
		Ni ₃ C							
#17	Ni ₃ C	Ni ₃ C	8343.6	-2.1 ± 0	1.93 ± 0.12	0.047 ± 0.044	-2.1 ± 2.2	2.62 ± 0.03	0.016 ± 0.003
#4		Ni ₃ C	8342.5	0.6 ± 0	1.79 ± 0.21	0.172 ± 0.259	0.6 ± 1.3	2.65 ± 0.03	0.016 ± 0.004
Ni ₃ C		Theory	8333.0	0	1.86		0	2.63	

Table 12: Calculated XRD data obtained by POWDERCELL by changing the lattice constants of the unit cell. For further calculation parameters see table 8.

		fcc-Ni	Ni ₃ C	Ni ₃ C (PSI)
unit cell change		-0.25%	+0.4%	+1%
C-Ni	bond		1.8683 Å	1.8795 Å
length				
Ni-Ni	bond	2.4855	~2.6389	~2.6575
length		Å	Å	Å
Position at 2Θ in °				
Peak #1		44.6	39.4	39.1
Peak #2		52.0	41.7	41.5
Peak #3		76.6	44.8	44.5
Peak #4		93.2	58.7	58.4
Peak #5			71.4	70.9
Peak #6			78.4	77.8
Peak #7			86.3	85.7
Peak #8			88.4	87.7
Peak #9			99.4	98.6