Supporting Information to:

In-situ Observations of Phase Transitions in Metastable Nickel(-Carbide)/Carbon Nanocomposites

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Experimental Details

Nanocomposite thin film deposition

Nickel(-carbide)/carbon nanocomposite thin films (~260 nm thickness) were sputter deposited with a dual target ionized magnetron sputter deposition system.[1] The sputter targets and the substrate holder were parallel to each other with a target-substrate distance of ~6 cm. Two independent targets (55 mm × 35 mm) were utilized: carbon (99.95% purity, 1 mm thick graphite, Goodfellow Limited) and nickel (99.99% purity, 1 mm thick Ni foil, Advent Limited) at 5.18 W cm^{-2} and 0.26 W cm^{-2}, respectively, with the power supplies operating in constant voltage mode. A 2½ turn copper coil, placed between the magnetrons and the substrate holder, was employed to generate a secondary inductively coupled plasma using a 13.5 MHz RF power supply. As the secondary plasma raised the target current by around 15%, the voltage was altered to ensure constant power. Base pressure of the deposition system was 1×10^{-7} mbar, and deposition was undertaken in 2×10^{-2} mbar argon (99.999%). The substrate holder was negatively bias at −150 V, as this has been previously shown to induce deposition of metastable Nickel-carbide.[1] No intentional substrate heating was applied. From control measurements with a thermocouple at the sample location it was confirmed that the plasma did heat the substrates to less than 120 °C during deposition i.e. samples remained during deposition below the here in-situ studied temperature range (150 °C to 800 °C).

Substrates for Nickel(-carbide)/carbon nanocomposite thin films sputter deposition were r-plane cut sapphire crystals for in-situ experiments. Reference films were also

deposited onto native oxide covered Si(100) wafer pieces, which were however not further annealed due to possible Si diffusion.[2] Post deposition samples were transported and stored in ambient air.

Ex-situ characterization and ex-situ annealing

Scanning electron microscopy (SEM) was undertaken with a Zeiss Sigma VP at 5 kV and using an Everhart-Thornley detector. Film composition was determined to ~30 atom-% C and ~70 atom-% Ni using energy dispersive X-ray spectroscopy (EDX, Zeiss Supra 55 VP at 20 kV with Oxford Instruments EDX detector). Transmission electron microscopy (TEM, 200 kV) employed a JEOL200FX, a FEI Technai TF20 FEGTEM and a Philips CM200, for which cross-sectional samples were prepared by focused ion beam milling.[3] A combination of bright field (BF) TEM and selected area electron diffraction (SAED) data was acquired. SAED data was further analyzed using PASAD software[4] which was also used to extract radially integrated SAED profiles. Ex-situ Raman spectroscopy measurements employed a custom-built setup with a laser excitation wavelength of 532 nm. The employed laser power was checked to not induce modifications to the sample during measurements. All point-localized ex-situ measurements were checked at least on three macroscopically separated spots across samples to ensure homogeneity of samples and representativeness of results. Ex-situ and in-situ annealed samples were also crosschecked with ex-situ XRD either in the below described in-situ XRD setup or in a Bruker D8 (CuK_{α}).

Ex-situ annealing of samples was undertaken in a custom-built vacuum chamber (base pressure 10^{-6} mbar) using a resistive boron nitride coated heater. Temperature was controlled using a combination of thermocouples and pyrometric measurements. After annealing natural cooling of the sample (~100 °C/min initial cooling rate) was employed. Estimated uncertainty for the quoted temperatures for the ex-situ anneals is ±10 °C. Post ex-situ annealing samples were transported and stored in ambient air.

In-situ measurements

In-situ XRD:

In-situ X-ray diffraction (XRD) was measured at the European Synchrotron Research Facility (beamline BM20/ROBL) using a X-ray wavelength of 1.078 Å in a previously described setup.[5–7] A cold-wall vacuum chamber (base pressure 10^{-5} mbar) is mounted onto a high-precision 6-circle goniometer. A resistive heater (Boralectric) was used for global sample heating where in-built and sample-surface-clamped thermocouples were used to control the sample temperature. We employed a grazing incidence X-ray diffraction geometry with an incident angle of 2°, thus largely suppressing strong reflections from the single crystalline sapphire substrates. The estimated information depth is ~200 nm.[8] Subsequent to annealing samples were left to cool naturally (~100 °C/min initial cooling rate). Estimated uncertainty for the quoted temperatures is ±40 °C. We note that all diffractograms show a step in intensity at ~18° which is related to the arrangement of detector and X-ray entrance/exit slits into the reaction chamber. For XRD data analysis the following Inorganic Crystal Structure Database (ICSD) entries were used fcc Ni: 646089, Ni_3C: 17005, graphite: 53781.

In-situ Raman spectroscopy:

We used a previously described in-situ Raman setup in which the Raman probe laser is concurrently used for sample heating.[9–11] Laser-induced annealing was undertaken in a vacuum of ~10^{-5} mbar. A laser (continuous wave [cw], 532 nm) is focused on the front side of the sample (front-illumination) to a 1 µm spot size (full-width-at-half-max [fwhm], measured using a knife-edge) with a 50× long-working-distance microscope objective through a viewport (for which it is optically compensated). For in-situ annealing experiments, the laser power was increased stepwise while measuring time-resolved Raman spectra (acquisition time 0.5 s) on a constant spot on the sample. We find that for laser powers up to 15 mW we do not observe any modification of the sample, thus allowing us to non-destructively probe the samples at these low powers. With increasing laser power we then find an evolution in the Raman spectra, indicating a rise in temperature. We find that for each step-wise power increase (up to 75 mW) the Raman background signal commonly stabilizes within the first few spectra, indicating that on the small heated spot equilibrium is quickly reached. As the laser both probes and heats the sample, the measured intensity in the raw data is a complex convolution of Raman scattering from temperature dependent phase contributions as well as the incident laser intensity. To eliminate the effect of incident laser intensity, normalization of the Raman spectra was employed here, where the measured raw Raman intensity was divided by the applied laser power. Only such normalized in-situ Raman data is plotted here. Subsequent to step-wise annealing samples were left to cool naturally. For estimation of temperatures from laser-induced heating see below. Raman spectroscopy information depth for such nanocomposite films is typically estimated at ~100 nm.[12] For analysis of Raman data (Figure 4d) we fitted single Lorentzians to the D, G and 2D regions. To estimate the lower bound of the in-plane-ordering size $L_a$of the nanocrystalline graphite we used the ratio $I(D)/I(G)$ of the intensities of the D and G peak following ref. 13 via the equation:

$$L_a = C \times \left(\frac{I(D)}{I(G)}\right)^{-1}$$

where the proportionality constant $C \approx 4.4$ nm.

In-situ XPS:

In-situ X-ray photoelectron spectroscopy (XPS) was performed at the ISISS beamline of the FHI/MPG located at the BESSY II synchrotron facility in Berlin, Germany.[14] The spectra were collected in normal emission in vacuum (10^{-7} mbar) and with a probe size of ~ 100 µm x 1 mm. The samples were heated from the back using an external IR-laser (cw, 808 nm), where temperature was applied homogeneously to the sample via a SiC spacer. The temperature was controlled via a K-type thermocouple in direct contact with the sample surface. Subsequent to annealing samples were left to cool naturally (~100 °C/min initial cooling rate). Estimated uncertainty for the quoted temperatures is ±40 °C. The Ni2p and C1s scans were acquired at X-ray incident energies of 1350 eV and 725 eV, respectively, thus yielding kinetic energies of 490 eV and 440 eV, respectively. This results in an electron mean free path of λ

~1.2 nm, thus giving an estimated information depth ($3 \times \lambda$) of ~3.6 nm,[15] although we note that precise determination of information depths in electronically heterogeneous composites (such as comprised of Ni and C, as here) is challenging. We emphasize however that, compared to Raman spectroscopy and XRD with information depths in the 100-200 nm range, our XPS signal is by relative amounts much more (sub-)surface sensitive. The estimated information depth of ~3.6 nm also suggests that effects from surface oxidation and adventitious carbon contamination from sample storage in ambient air are minimized.[16] For XPS analysis, the photoelectron binding energy (BE) is referenced to the Fermi edge, and the spectra are normalized to the incident photon flux. Background correction was performed by using a Shirley background.[17] The spectra were fitted following the Levenberg-Marquardt algorithm to minimize the χ^2. Peak shapes were modelled following Blume et al.[18] The accuracy of the fitted peak positions is ~0.05 eV.

Comment on estimation of temperatures

The most accurate temperature estimation of ±10 °C during vacuum annealing was achieved for the ex-situ anneals via careful cross-calibration using a combination of thermocouples clamped to the sample surface and the substrate holder as well as pyrometric measurements. In contrast, the in-situ XRD and in-situ XPS measurement have larger estimated uncertainties in temperature of ±40 °C, while the in-situ Raman measurements did not provide any reliable temperature measurements of the local temperature at the 1 μm laser spot. Therefore, in order to confirm quoted in-situ XRD and XPS temperatures and calibrate estimated temperatures for localized in-situ Raman heating as function of applied in-situ Raman laser power, we employed ex-situ Raman measurements on all in-situ treated samples and used the thus observed degree of carbon ordering (G peak width, I(D)/I(G), I(2D)/I(G)) as an internal calibration against ex-situ annealed samples. Thereby, in-situ Raman measurements were estimated to locally yield ~300 °C at 35 mW and ~700 °C at 85 mW applied laser power, respectively and the quoted in-situ XRD and XPS temperatures were confirmed. We note that this temperature estimation for the in-situ Raman measurements is also in good agreement with previous studies which showed a linear increase of the local laser-heating-induced temperature rise with respect to the applied laser power.[11,19] We estimate an uncertainty of the quoted in-situ Raman temperatures of ±50 °C.

Comment on Ni_3C phase assignment

There is a long standing debate in the literature on the notorious difficulty to assign the presence of carbon-containing Ni_3C (space group: $R\bar{3}c$; ICSD 17005) with certainty with respect to the potential presence of a largely isostructural carbon-free hexagonally closed packed (hcp) Ni phase (space group: $P6_3/mmc$).[20–23] This difficulty arises from the fact that both phases consist of a hcp Ni (sub-)lattice, which in the case of Ni_3C has an *ordered* sublattice of interstitial carbon added.[20] The added ordered interstitial carbon does however only slightly change the resulting diffraction patterns which is why SAED or XRD routinely exhibit difficulties in assigning either phase with certainty. This picture is further complicated since recent reports[20,21] suggested the formation of *carbon-containing* hcp Ni (termed hcp-NiC_y) which differs

with respect to Ni_3C only in terms of decreased interstitial carbon ordering i.e. hcp-NiC_y is a disordered form of Ni_3C. In contrast, previous work showed that even trace carbon contamination in hcp Ni formation processes will lead to the formation of Ni_3C.[20] Low angle diffraction measurements have been recently suggested to allow unambiguous identification of Ni_3C based on very low intensity superlattice reflections.[20–22] The sensitivity of our time-resolved in-situ XRD measurements under our processing conditions is however not high enough to either confirm or exclude the presence of these superlattice reflections. We however note that in the SAED measurement of the as deposited nanocomposite films (Figure 1b) we find indications of weak diffraction spots which could be assigned as the (104) superlattice reflection of Ni_3C. Presence of these reflections unambiguously proves the existence of Ni_3C and excludes hcp Ni.[20–22]

The presence of carbon-free hcp Ni in our as deposited films can be further excluded with confidence based on the following arguments: 1. It has been previously shown that even trace carbon contamination in hcp Ni formation processes will lead to the formation of Ni_3C[20] or at least its disordered form hcp NiC_y.[21] Given the overall carbon content in our films of ~70 atom-% C, carbon-free formation of hcp Ni is therefore excluded under our conditions. 2. We observe a very low binding energy signature (~283.0 eV) in the *carbon* C1s signature in XPS for the as deposited films and for anneals up to 300 °C. This low binding energy component has in previous literature[24] been assigned to crystalline Ni_3C. Also in our measurements its presence correlates directly with the presence of the suspected Ni_3C SAED and XRD patterns. Since this XPS signature is measured on the *carbon* C1s core level, its presence clearly excludes carbon-free hcp Ni, which due to lack of carbon would not show any corresponding C1s signal. Combined our observations fully exclude the presence of carbon-free hcp Ni and thus confirm the presence of a Nickel-carbide in our as deposited films. The weak (104) diffraction spots in the SAED pattern of the as deposited films give a good indication that this Nickel-carbide is indeed Ni_3C.

We note however that our general usage of the terms Nickel-carbide and Ni_3C in this manuscript not only includes fully ordered Ni_3C but may also include disordered forms of Ni_3C approaching the recently suggested[20,21] hcp NiC_y form (i.e. hcp Ni sublattice incl. somewhat disordered interstitial carbon).

Supporting Table 1 of possible XPS binding energy (BE) assignments

C1s BE/eV	***Possible assignments from literature***
284.9	Disordered carbon (with a certain fraction of sp^3-like bonding).[18,25]
284.4	sp^2 bonded carbon.[18,25]
283.7	Solid solution of carbon interstitially dissolved in metallic Ni[25] (here termed Ni(-C), where the comparably high BE indicates significant carbon dissolution). Also reported for Ni_3C.[26]
283.0	Crystalline Ni_3C.[24] (Ni_2C surface reconstruction on Ni(111) has also been reported but at a slightly higher binding energy of 283.2eV.[27])
285.5	Adventitious carbon adsorbates from sample storage in ambient air.[28,29]

Ni2p BE/eV	***Possible assignments from literature***
854.4 and >855	Oxidized Ni.[30]
853.4	Ni with carbon interstitially dissolved (Ni(-C)).[25] Also consistent with Ni_3C.[16,26,31]
852.4	Metallic Ni.[25]

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