Study of Ni-Catalyzed Graphitization Process of Diamond by in Situ X-ray Photoelectron Spectroscopy

O. Romanyuk, †‡ M. Varga, ‡ S. Tolic, † T. Izak, † P. Jiricek, † A. Kromka, † V. Skakalova, † and B. Rezek

†Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague 6, Czech Republic
‡Physics of Nanostructured Materials, Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria
§Faculty of Electrical Engineering, Czech Technical University, Technická 2, Prague 6, Czech Republic

ABSTRACT: Graphene on diamond has been attracting considerable attention due to the unique and highly beneficial features of this heterostructure for a range of electronic applications. Here, ultrahigh-vacuum X-ray photoelectron spectroscopy is used for in situ analysis of the temperature dependence of the Ni-assisted thermally induced graphitization process of intrinsic nanocrystalline diamond thin films (65 nm thickness, 50–80 nm grain size) on silicon wafer substrates. Three major stages of diamond film transformation are determined from XPS during the thermal annealing in the temperature range from 300 °C to 800 °C. Heating from 300 °C causes removal of oxygen; formation of the disordered carbon phase is observed at 400 °C; the disordered carbon progressively transforms to graphitic phase whereas the diamond phase disappears from the surface from 500 °C. In the well-controllable temperature regime between 600 °C and 700 °C, the nanocrystalline diamond thin film is mainly preserved, while graphitic layers form on the surface as the predominant carbon phase. Moreover, the graphitization is facilitated by a disordered carbon interlayer that inherently forms between diamond and graphitic layers by Ni catalyst. Thus, the process results in formation of a multilayer heterostructure on silicon substrate.

INTRODUCTION

Many promising technological applications of graphene need high-quality large-scale sheets to be synthesized. There are various methods for large area graphene synthesis, such as thermally induced growth on metal surfaces, thermal, plasma chemical vapor deposition, and thermal annealing of SiC surfaces. For device production, subsequent exfoliation of the graphene sheet and graphene transfer procedures are required. These procedures, however, often lead to increased contamination and defects in graphene sheets. These undesired side effects can be detrimental for the performance of graphene-based devices. Direct fabrication of graphene-on-diamond heterostructures is now being explored as a promising alternative technology.

Graphene and diamond exhibit extraordinary intrinsic properties [thermal conductivity ~3000 J/(K m) and mechanical modulus ~1 TPa] resulting from the C–C bonds which are related to the σ electronic states present in both crystal structures. In contrast, there is a significant difference in the electronic band structures of diamond and graphene due to the different electronic orbital hybridizations: sp³ in diamond and sp² in graphene. While graphene behaves as a semimetal having a linear dispersion relation, diamond is a large bandgap semiconductor with high electrical resistivity in the intrinsic form. Combining these two materials and their complementary properties in a single system denoted as graphene-on-diamond is opening new prospects for fundamental science and for applications.

A straightforward method for making graphene-on-diamond is the simple transfer of CVD-synthesized graphene on to a diamond surface. However, surface contamination by polymer residuals or acids cannot be completely avoided in this case. Another way is directly to graphitize the topmost diamond surface by annealing at high temperatures and at low pressure. In the past, the graphitization process has mainly been studied on well-defined monocrystalline diamond surfaces. Graphitization on a bare monocrystalline diamond C(111) surface began at approximately 850 °C, while for a bare monocrystalline diamond surface C(100) graphitization began at 1200 °C. Monocrystalline diamond substrates with a large surface area for graphene-on-diamond technology would be too costly for commercial applications. However, nanocrystalline diamond (NCD) offers an alternative, chemically matched native...
platform for graphene synthesis. The growth technology for large-area NCD layers by CVD methods is well established.\textsuperscript{15}

Graphene formation on a diamond surface can be promoted by metal catalysts. Metals such as Ni, Cu, or Fe are used to melt or dissolve carbon atoms\textsuperscript{16−19} and, therefore, to reduce the graphitization temperature of a diamond surface significantly. In particular, a graphitization temperature as low as 247 °C has been reported on Ni/C(100).\textsuperscript{14}

Recently, graphene synthesis on an Ni/ultrananocrystalline diamond (UNCD) film by rapid thermal annealing (RTA) has been demonstrated.\textsuperscript{8} The high-resolution C 1s spectrum measured on the graphene/UNCD surface was asymmetric. It was fitted by one (unspecified) function and assigned to the graphene-related component.\textsuperscript{8} The photoelectron emission from the UNCD substrate and disordered carbon by Ni have not been considered. However, photoelectron emission from the layers below a few graphene layers is expected.

Other recent papers dealt with Ni-enhanced graphitization of amorphous carbon films (a-C) prepared by CVD.\textsuperscript{20−22} The a-C/Ni films were annealed mainly in a hydrogen atmosphere. It was observed that carbon films exchange with Ni film and graphitizes at elevated temperature.\textsuperscript{23−25} Recent theoretical studies explained the graphitization mechanism for RTA: a-C to graphene transformation entails the metal-induced crystallization and layer exchange mechanism. Carbon dissolution in Ni was excluded.\textsuperscript{26}

In the present work, a detailed analysis of dynamic changes of carbon phases in an Ni/nanocrystalline diamond film with faceted diamond grains is carried out in situ as a function of annealing temperatures up to 800 °C under ultrahigh-vacuum (UHV) conditions, i.e., without a hydrogen atmosphere. We show that Ni-catalyzed graphitization considerably affects the NCD surface. X-ray photoelectron spectroscopy (XPS) data indicate a transformation of the diamond surface to disordered carbon at low temperatures and then, above 600 °C, to a graphitic/multilayer graphene phase covering the surface. Raman measurements confirm that diamond grains are preserved below the graphitized surface.

\section*{Experimental Section}

NCD thin films (about 65 nm in thickness) were grown on p-type Si (100) substrates with a native oxide layer. Before the growth process, the Si substrates were ultrasonically cleaned in acetone and isopropyl alcohol and were rinsed in deionized water. Then, the substrates were seeded by applying ultrasonic agitation in a nanodiamond colloid (NanoAmando aqueous solution 5.0% w/v; median nanodiamond size 4.8 ± 0.6 nm (98.8 wt %); dilution by deionized water 1:40 v:v). The diamond growth was performed by focused microwave plasma chemical vapor deposition (MW-CVD), using an ellipsoidal cavity resonator from a hydrogen and methane gas mixture (98.8 wt %); dilution by deionized water 1:40 v:v). The a-C/Ni films were annealed in a hydrogen atmosphere.

The thickness of the NCD film was about 800 °C during the growth.

As-grown NCD samples were transferred from the MW-CVD reactor to the metal evaporation chamber. A layer of 20 nm Ni was evaporated on top of the NCD films at room temperature. The Ni/NCD samples were then further transferred to the AXIS Supra X-ray photoelectron spectrometer (Kratos Analytical Ltd., UK). The Ni/NCD samples and the reference NCD sample were sequentially annealed and cooled down to room temperature in an analytical XPS chamber under UHV. The sample temperature was increased up to 800 °C in 100 °C steps in 20–30 min intervals. The pressure in the XPS chamber was kept below 10\textsuperscript{−7} mbar during the XPS measurements.

Survey XPS spectra and high-resolution C 1s, O 1s, and Ni 2p\textsubscript{1/2} core level spectra were measured using monochromatized Al Kα radiation (1486.6 eV, probe area is 0.7 × 0.3 mm\textsuperscript{2}). Photoelectrons were collected in constant energy mode with a pass energy of 10 eV, resulting in overall energy resolution of 0.45 eV, measured on the Ag 3d\textsubscript{5/2} line width. The X-ray incidence angle was at 54.4° with respect to the surface normal, and XPS spectra were measured at the normal emission angle. All samples were sufficiently conductive, so charge compensation was not used during XPS spectra acquisition.

The chemical composition of the film surface was determined from the corresponding photoelectron peak areas after standard Shirley inelastic background subtraction and using the relative sensitivity factor method. The high-energy resolution core level peaks were analyzed by peak fitting applying a few sets of line shape functions: Doniach–Sunjic (DS) line shapes\textsuperscript{27} convoluted with Gaussian functions were used as primary fit functions, and Voigt functions were used as a secondary set of functions in order to estimate the reliability of the fits. The two function sets provided similar results. As DS functions are more suitable for the analysis of graphite and graphene layers,\textsuperscript{28,29} they are also preferred here.

The shape of the DS function was derived independently by measuring the C 1s peak on cleaved highly oriented pyrolytic graphite (HOPG). A commercially available HOPG sample (MikroMasch company) was 10 × 10 × 1 mm\textsuperscript{3} in size and was of ZYB grade (mosaic spread: 0.8°). The HOPG sample was attached to the sample holder by two-sided Scotch tape. In order to obtain a fresh, clean surface of the HOPG, the thin upper layer of the sample was removed using a razor blade just before the HOPG sample was inserted into the flexi-lock chamber of the photoelectron spectrometer. A negligible amount of oxygen contamination was confirmed on the freshly cleaved HOPG surface by XPS. The high-resolution C 1s experimental data and the corresponding fitted DS function are presented in the Supporting Information (Figure S1 and Table S1).

The surface morphology of the diamond films was analyzed using a Tescan MAIA3 field-emission scanning electron microscope (SEM) equipped with an in-beam secondary electron detector and back-scattered electron detector (BSE). The thickness of the NCD film was evaluated from the interference fringes in the reflectance spectra measured in the range of 400 nm–1000 nm.

Raman spectra were measured using a Renishaw In Via Reflex Raman spectrometer with an excitation wavelength of 442 nm (He–Cd laser). The exposure time was set to 60 s, while the output power of the laser was decreased to 10% (∼1 mW) to minimize the heating effect of the laser beam. All spectra were measured in a backscattering setup with a 100× objective in the confocal mode with a grating of 2400 lines/mm and with a corresponding spectral resolution of 1.2 cm\textsuperscript{−1}. The laser spot was approximately 5 μm in diameter.

\section*{Results and Discussion}

Figure 1a shows a typical top-view SEM image of the as-grown NCD films.\textsuperscript{30,31} The diamond grains are clearly recognized. Grain sizes vary from 50 nm to 80 nm. Figure 1b shows that the evaporated 20 nm thick Ni layer conforms to the primary NCD
surface morphology. Only the slightly smoothed grain edges and the homogenized secondary electron emission are noticeably different. Figures 1c and 1d show the representative surface morphology of the Ni/NCD sample after thermal annealing to 600 °C and 800 °C, respectively. There are black protrusions that have appeared in Figures 1c, but the Ni/NCD film morphology is similar to the as-received Ni/NCD sample in Figures 1b. The surface morphology becomes overall flatter and smoother in Figures 1d: NCD grains are no longer recognized. Some cracklike dark features with bright edges appear on the film surface. The SEM features are corroborated by XPS analysis: XPS revealed no sp³ bond contributions of NCD grains on the annealed Ni/NCD surfaces.

Figures 1e and 1f show 45° view SEM images of the Ni/NCD annealed at 600 °C measured in secondary electron and BSE modes, respectively. The SEM image (Figure 1e) shows the surface morphology, whereas the SEM-BSE image (Figure 1f) reveals the difference in the chemical composition on the same area.

The Ni-contained layers and particles are the brightest, the pure carbon phases are the darkest, and in between the composition of “C/Ni” phases is present. This could be explained by additional carbon layers on top of Ni layers. As will be shown later, the “C” phase could correspond to the disordered or graphitic phase of carbon.

The dependence of the surface chemical composition on the annealing temperature was measured in situ by XPS. It should be mentioned that the probe depth is limited due to photoelectron attenuation in solids. For the particular core level energies, the photoelectron inelastic mean free path is around 1.6 nm–2.6 nm, which limits the photoelectron escape depth to about 3–7 nm. In addition, surface composition measurements can be affected by surface roughness, especially for angle-resolved XPS. We verified this effect on samples with different grain sizes. For normal photoelectron emission, however, the effect of surface roughness was found to be negligible.

Figure 2a shows the dependence of C, Ni, and O atomic concentrations on the annealing temperature obtained from the integrated core level XPS peak intensities. The as-prepared Ni/NCD film consisted of oxide layers on the surface. It is expected that the as-received Ni/NCD film is contaminated by O and Ni oxide layers, as the sample was exposed to air while it was being transferred to the XPS chamber. In our case, the O 1s

Figure 1. SEM secondary electron images of (a) the as-grown NCD film, (b) the NCD film coated with a 20 nm Ni layer, (c) the Ni/NCD sample annealed at 600 °C, and (d) annealed at 800 °C and cooled down to room temperature. SEM images of the partially delaminated region of the Ni/NCD annealed at 600 °C and measured under a 45° angle in (e) secondary electron mode and (f) in backscattered electron mode.

Figure 2. (a) Dependence of atomic compositions in the near-surface region of the samples on the annealing temperature obtained from the integrated core level XPS peak intensities. (b) Dependence of the C 1s core level peak maxima on the annealing temperature. Cleaning, disordering, and graphitization stages are marked by white, blue, and green colors of the background, respectively.
core level peak involved two components, which are related to the C−O and Ni−O bonds (Figure S3 in the Supporting Information). Oxygen and Ni oxide almost disappeared from the Ni/NCD surface at 300 °C. The increase in Ni relative concentration up to about 68 at. % at 300 °C can therefore be attributed to the removal of surface contamination. In contrast to Ni, only a small decrease in carbon concentration is observed at 300 °C. The carbon signal must therefore have originated from the NCD grains underneath the Ni thin film. The NCD surface is rough, and it could happen that the Ni coverage is not uniform on grain facets and grain boundaries or that there are cracks in the Ni layer.

The Ni atomic concentration drops to less than 1.0 at. % at 700 °C (close to the detection limit of the XPS method), so Ni disappeared from the surface. As the temperature is too low for Ni evaporation (its melting point is 1455 °C), Ni atoms must be diffusing from the surface toward the bulk, as discussed below. At the same time, the carbon concentration at the surface increases steadily and reaches 99 at. % at 700 °C.

In Figure 2b, the C 1s peak maximum position moves from 285.4 eV at room temperature to a lower binding energy of 284.9 eV at 300 °C. Between 300 °C and 500 °C, the C 1s peak position moves back to higher binding energies. Finally, at a temperature of 500 °C the C 1s again moves back toward lower binding energies. The change in the C 1s peak position correlates with the changes in atomic concentrations on the surface (as indicated by the colored background). Peak shifts are caused by the formation of new carbon phases on the sample surface during the annealing process.

Figure 3 shows the temperature dependence of high-resolution Ni 2p3/2 XPS spectra. XPS spectra below 300 °C (during oxygen desorption) are shown in the Supporting Information. Oxygen desorption33 up to 300 °C did not have a crucial impact on graphitization. At temperatures above 300 °C, the Ni 2p3/2 peak position (852.9 eV) and the Ni energy loss peak position (858.8 eV) agree well with the corresponding energy position values for an Ni film prepared by sputtering.33 At temperatures higher than 700 °C, the photoelectron emission from the Ni atoms dropped to the background level: the Ni atomic concentration decreased to less than 1 at. % on the sample surface, as shown in Figure 2a.

In contrast to the C 1s peak position maxima (Figure 2b), the Ni 2p3/2 peak position maxima remain constant during annealing (Figure 3). In addition, the C−Ni peak components at low binding energies (283.3 eV)34,35 are not present on the C 1s spectra. These results have two fundamental implications. First, the shift of the C 1s peak position with temperature is not caused by band bending or by surface charge effects (the Ni peak position is constant). It must therefore be related to the change in the chemical state of the original diamond bonds at the surface. Hence, the phase transition takes place during the annealing process. Second, the XPS data confirm that Ni does not react chemically with carbon atoms and indeed serves as a catalyst facilitating sp3 to sp2 carbon phase transformation at the diamond surface.

Figure 4 elucidates this transformation by fitting the high-resolution C 1s core level peak measured on the Ni/NCD sample at different annealing temperatures (the C 1s spectra below 300 °C were not included here, since a study of oxide desorption is beyond the scope of the present paper). The C 1s peak positions, the peak component widths, and the asymmetry factors of DS functions for all annealing stages are given in the Supporting Information (Table S1). The fluctuation in binding energy of ±0.1 eV is possibly due to a finite data acquisition energy step of 0.1 eV and due to the error bar of the fitting procedure.

The C 1s peak at 300 °C and 400 °C involves a dominant sp3 component and a few percent of sp2 component. The sp3 peak position (284.9 eV) and the sp2 peak position (283.8 eV) agree well with the corresponding values of the C 1s core level peak positions for an NCD surface.36 It should be emphasized, however, that the C 1s peak maxima can vary for different forms of carbon with different types of bond hybridization and surface contamination (C−O bond concentration) or with the surface charge effect (especially for an undoped semiconductor). The sp3 to sp2 component energy difference of around 0.9 eV−1.1 eV (as also observed here) is thus a more reliable characteristic of NCD films.36 A few percent of oxygen still remains on the surface after annealing at 300 °C (see also Figure 2a), but most of the photoelectrons originate from the NCD film at this temperature.

The C 1s peak maximum is shifted to the direction of higher binding energy between 400 °C and 600 °C. The shift is caused by the Cdis component at 285.2 eV. At higher temperatures (T > 700 °C), another G component at 284.8 eV is responsible for the C 1s peak maxima shift backward to lower binding energies. Since the C 1s binding energy positions vary in the literature for different carbon phases and experimental conditions, it is not straightforward to identify the particular component. In order to identify the components, component peak shape analysis (asymmetry of the peak) and Raman measurements of the annealed Ni/NCD samples were carried out.

Typically, symmetric Gaussian or Lorentzian functions, or a combination of them, are used for deconvolution of high-resolution C 1s spectra measured on NCD, on diamond-like carbon (DLC), or on amorphous carbon films. The C 1s peak of clean, contamination-free conductive carbon films such as HOPG, graphene, or graphitic films is asymmetric.28 In this case, the asymmetry of the C 1s peak is related to the shake-off.
In addition, the asymmetry is not due to oxygen bond contributions. In contamination on the Ni/NCD samples, and the spectra temperatures higher than 400 °C there would be no oxygen contamination on the Ni/NCD samples annealed at high temperatures (see Supporting Information). Therefore, a dominant asymmetric component of the C 1s peak at 284.8 eV was identified as originating from graphitic (G) layers. The presence of graphitic layers on the Ni/NCD samples annealed at high temperature was also confirmed by Raman measurements, as discussed below.

In contrast to the G components, the C_{dis} components at 285.2 eV are symmetric (α = 0.0), and π-plasmons were absent in C 1s spectra up to 600 °C. This component was attributed to the disordered carbon (also supported by the D-band peak in the Raman spectra below). A similar energy difference of 0.4 eV between the graphene component (Gr) and the “deleterious” phase of carbon (C_B) has been measured previously during graphene growth on Ni by the CVD method. The C_B component has been identified as an sp^3-related component, which is questionable since no diamond (sp^3) peak is present in the Raman spectra there. However, the C_B component can be correlated with the D-band peak in the Raman spectra similar to our case, and the C_B component is related to disordered carbon rather than to the diamond. Our XPS measurements therefore confirm that Ni amorphizes the NCD surface during its diffusion into the NCD film; i.e., disordering by Ni catalysis occurs prior to surface graphitization.

The disordered carbon phase concentration further increases with respect to the NCD phase concentration with increasing temperature. At 500 °C, the C 1s peak consists of a dominant C_{dis} component, whereas the sp^3 and sp^2 components of the NCD films are absent although some NCD areas can be seen rarely on SEM images close to defects (the NCD fraction is below the detection limit of XPS). Therefore, Ni amorphizes the NCD film drastically rather than “gently” diffusing into the NCD film through its grain boundaries. In addition to the disordered carbon peak component, the G component at 284.8 eV appears at 500 °C. This temperature seems to be crucial for graphitic layer formation on a disordered NCD surface. The concentration of the graphitic phase, i.e., the area of the G component, further increases with increasing annealing temperature up to 700 °C.

The position of the G component at 284.8 eV is somewhat different from the position of the graphene component at 284.4 eV in the literature, but it is closer to the corresponding C 1s peak position of 284.6 eV measured here on HOPG (see Supporting Information) and on graphene/UNCD. In addition, the full width at half-maxima (FWHM) of the G component and the asymmetry factors are quite similar to the corresponding parameters of the C 1s peak measured on HOPG. The 0.2 eV difference in G peak position could therefore be related to the quality of the film or to the number of graphene/graphitic layers.

In Figure 5, the sp^2/sp^3 component area ratio (red spheres) and the G/C_{dis} component area ratio (green squares) are shown as a function of the annealing temperature. At lower annealing temperatures, 6% of the sp^2 bonds and 92% of the sp^3 bonds were derived on the Ni/NCD surface (the ratio is 0.06). The disordered carbon phase concentration is higher than the graphitic phase concentration up to 600 °C. At temperatures of 700 °C and higher, the ratio G/C_{dis} is greater than 1, indicating graphitization of the disordered phase on the surface. When the sample is cooled back to room temperature, the G/C_{dis} ratio decreases slightly, most likely due to reordering of carbon atoms on the surface. In any case, the coexistence of graphitic and disordered carbon phases is well recognized on the surface.

**Figure 4.** Temperature dependence of the high-resolution C 1s core level peaks measured on the Ni/NCD surface by XPS. The experimental data are marked by dots, the fitted spectra are marked by solid black lines, and the component envelopes are marked by filled color lines. The C 1s peaks consist of sp^3 (red) and sp^2 (blue) components of the NCD substrate at 300 °C and at 400 °C; disordered carbon (C_{dis} cyan) is present at 400 °C; the graphitic phase component (G, green) appears at T > 500 °C. The concentration of the graphitic phase is indicated as a relative percent.
In summary, XPS analysis confirmed the formation of disordered and graphic phases on Ni/NCD surface at \( T > 500 \) \(^\circ\)C. This finding can be correlated with SEM observations. In Figures 1c, 1e, and 1f, a new carbon phase, "C", is present which could be related to the disordered and/or graphic phase according to XPS measurements (see C\(_{\text{dis}}\) and G components in C 1s spectra).

The "C/Ni" phase covered the sample surface almost completely at 600 \(^\circ\)C, and only a few spots of pure "C" phase were present. Since the atomic concentration of Ni was about 30 at. % only for 600 \(^\circ\)C (Figure 2a), the "C/Ni" phase thus corresponds to the Ni layers covered by carbon phases. In other words, melted disordered carbon atoms have to diffuse from the Ni/NCD interface upward to the Ni surface.

Figure 6 shows Raman spectra of the reference NCD sample annealed at 800 \(^\circ\)C (without Ni) and the Ni/NCD samples annealed at 600 \(^\circ\)C and 800 \(^\circ\)C. For the reference NCD sample (red curve), there are two dominant peaks: a sharp diamond peak at 1331 cm\(^{-1}\), which is attributed to diamond bonds, and a broad band at \( \sim 1560 \) cm\(^{-1}\) (a mixture of sp\(^3\)/sp\(^2\) carbon bonds). In addition, there is a small band at 1150 cm\(^{-1}\), which is characteristic for NCD, and it is attributed to trans- polyacetylene-like groups.\(^{40}\) The Raman spectrum of the as-grown NCD, i.e., before annealing, is not shown here, as it is similar to the Raman spectrum of the reference annealed NCD sample. Thus, the bare NCD film is rather stable during annealing up to 800 \(^\circ\)C in UHV.

In contrast to the reference NCD Raman spectrum (Figure 6, red curve), the spectrum of the annealed Ni/NCD at 600 \(^\circ\)C contains an additional so-called D-band (defect band) peak at 1370 cm\(^{-1}\) and a small G-band (graphic) peak\(^{41,42}\) at 1582 cm\(^{-1}\) (Figure 6, green curve). The D-band peak is related to a disordered carbon phase, and G-band is related to a graphic phase. It agrees with the XPS findings of the C\(_{\text{dis}}\) and G components of the C 1s peak.

The D-band peak intensity is enhanced relative to the diamond peak intensity at a higher temperature (black curve, 800 \(^\circ\)C). Therefore, more defects in NCD are present at higher annealing temperatures. In addition, the sharp graphite G-band at 1582 cm\(^{-1}\) and the 2D-band at 2740 cm\(^{-1}\) are present in the Raman spectrum at 800 \(^\circ\)C. A diamond peak is also observed at 1331 cm\(^{-1}\), reflecting the presence of retained NCD grains. Its intensity is lower than in the G-band and 2D-band peaks, however. The intensity ratio of 2D/G is about 0.5, which corresponds to multilayered graphene or thick graphic layers, rather than to a single graphene layer.\(^{3}\) It should be noted that the underlying NCD film was not measured by XPS due to the limited escape depth of the photoelectrons. In the case of Raman measurements, the probe depth is significantly larger, and a NCD film was clearly observed beneath the graphic phase. Thus, a sequence of carbon phase transformations during the Ni catalytic reaction on the Ni/NCD samples was identified by Raman measurements. The D-band appears prior to the G-band and 2D-band during annealing, which is in line with \textit{in situ} XPS results.

A schematic diagram of the annealing process is shown in Figure 7. The Ni layer becomes free of oxide and contaminations at temperatures higher than 300 \(^\circ\)C (Figure 7a). The Ni layers melt the NCD film at the Ni/NCD interface, and disordered carbon diffuses onto the Ni layer surface and partially graphitizes in (c). Disordered carbon recrystallizes to graphic phase at a high annealing temperature (d).
According to Raman measurements, the NCD film was partially preserved, and according to the XPS measurements, the Ni film disappeared from the surface and thus has to be embedded beneath the surface carbon layer.

**CONCLUSIONS**

Step-by-step graphitization of an NCD thin film surface was thermally induced by Ni-catalyzed reactions and was investigated in situ by XPS. Several phase transitions during thermal annealing were revealed. Deconvolution and a detailed analysis of the high-resolution C 1s spectra measured during the annealing process revealed disordering of the NCD surface above 300 °C. Graphitization starts at 500 °C, and the graphitic-to-disordered C phase ratio increases with increasing temperature. At 700 °C, the fraction of the graphitic phase became about 1.75 times higher than the fraction of the disordered C phase. Diamond was not preserved on the surface while the Raman spectra still con...
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