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Carbon films grown on Pt(1 1 1) as supports for model gold catalysts

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Abstract

Carbon films were grown on a Pt(1 1 1) single crystal by ethylene decomposition at elevated temperatures (1000–1300 K). Depending on the preparation conditions, different carbon structures formed on the metal surface such as flat and curved graphitic layers, carbon particles and carbon nanowires. Although these carbon films exhibited a high density of surface defects, gold interacted only weakly with the carbon surface. CO adsorption on the Au/carbon systems was very similar to that observed for various Au/oxide systems previously studied. This finding strongly indicates that CO adsorption on gold is essentially independent of the nature of support.

Keywords: Carbon; Thin films; Nanocarbon; Gold

1. Introduction

The interaction between a gold particle and its support is believed to play an important role in the catalytic properties of the particle, particularly for low temperature CO oxidation (see reviews [1–3]). The supports involvement is manifested in numerous ways including direct participation in the reaction or through stabilization of the active gold species. In order to elucidate reaction mechanisms in these complex systems surface science studies employ model systems providing at times an atomic level description of reaction processes. Most of these studies have been performed by depositing gold onto *oxide* single crystals and thin films ([3–8] and references therein). For *carbon* supported model catalysts, highly oriented pyrolitic graphite (HOPG) is typically used as a substrate. However, the interaction of gold with the graphite basal surface is weak, resulting in the formation of large metal particles preferentially located at the step edges (see recent review [9]). A consequence of this weak interaction is that structural studies of Au nanoparticles using scanning tunneling microscopy (STM) are very difficult due to tip induced displacement of the particles. In order to form and stabilize smaller particles and circumvent these difficulties, ion pre-sputtered graphite surfaces have been suggested as model carbon supports [9–11].

We believe that an alternative approach could be the growth of carbon films on metal substrates potentially allowing greater control of the defect structure on the carbon surface. It has been well documented in the literature, that carbon overlayers can be formed on many metal surfaces such as Ni and Pt through the decomposition of hydrocarbons [12–15]. In most cases, the resulting carbon overlayer is graphitic in nature and exposes the basal (0 0 0 1) plane. The formation of graphite islands on Pt(1 1 1) has been shown directly using STM by Land et al. through the heating of pre-adsorbed ethylene to 800 K [16]. Upon further heating to 1000 K, the graphite islands coalesced. More recently, however, Pazhetnov et al. [17] have suggested that carbon films on Pt surfaces at elevated temperatures (>1200 K) may exhibit graphene layers with strongly bent surfaces similar to those in fulle-

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renes and nanotubes. Since the interaction of metal atoms with carbon surfaces is predicted to depend on the curvature of a graphite sheet [18], one expects that the nucleation and growth of metal particles on these carbon supports would differ significantly from HOPG, which in turn might affect their reactivity.

In this paper, we have studied the structure of the carbon films formed on Pt(1 1 1) at high temperatures (1000–1373 K) as well as the structure of gold particles deposited on these films using STM and X-ray photoelectron spectroscopy (XPS). Further, temperature programmed desorption (TPD) was used to study the adsorption properties of both the carbon and Au/carbon systems. Our results do not show any preferential nucleation of the Au particles along the curved graphite surfaces. In addition, the TPD results are quite similar to the results for CO adsorption on oxide supported Au particles, therefore suggesting that the adsorption of CO on Au is independent of the nature of the support.

2. Experimental

The experiments were performed in two UHV chambers (base pressure $<5\times10^{-10}$ mbar). One (the "STM" chamber in Berlin) was equipped with STM, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a differentially pumped quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD) measurements. The other (the "XPS" chamber in Novosibirsk) was equipped with a VG ESCALAB spectrometer, LEED and QMS.

The Pt(1 1 1) crystal was cleaned by numerous cycles of Ar sputtering and annealing at 1300 K. Traces of surface carbon were removed by oxidation in 10^{-6} mbar O_2 at 600 K followed by flashing to 1000 K. The resulting surface had very sharp LEED diffraction spots characteristic of Pt(1 1 1). Also, neither AES nor XPS showed any impurity signals.

Following the procedures reported in Ref. [17], the low temperature (LT) carbon film was formed on Pt(1 1 1) by exposure to 10^{-7} mbar of ethylene at 300 K followed by heating to 1000 K with the rate 3 K/s and keeping the sample at this temperature for 30 min. After heating was switched off, the sample was cooled in ethylene ambient down to 800 K before pumping out the ethylene. The high temperature (HT) carbon film was prepared as follows. The sample was exposed to 10^{-7} mbar of ethylene at 300 K for 3 min, heated up to 1173 K with the rate 3 K/s and kept at this temperature for 5 min followed by slow (0.05 K/s) heating to 1373 K where the sample was kept for 5 min before slowly cooling down (−0.03 K/s) to 800 K and pumping out the ethylene.

In the "STM" chamber, Au was deposited from a Au-filled Mo crucible, with a deposition rate of ca. 0.1 Å/min. In the "XPS" chamber, Au was deposited from a Au wire wrapped around a W-filament. For TPD measurements (performed in the "STM" chamber), the sample was placed ~1 mm from the nozzle of the QMS and heated at a rate of 5 K/s. All high purity gases were dosed via a calibrated directional doser.

STM images were obtained with Pt–Ir tips at typical tunneling parameters of $V = 20$–100 mV and $I \sim 1$ nA on carbon films, and $V \sim 0.1$–3 V and $I \sim 0.1$–0.5 nA on the Au/carbon samples. The images were essentially independent of the bias polarity. The images presented in the paper were subjected to plane correction and low pass filtering.

XPS spectra were recorded using Al Kα radiation ($h\nu = 1486.6$ eV) and analyzer pass energy 20 eV. The binding energies were referenced to the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.7 eV) values.

3. Results and discussions

3.1. Surface morphology of the carbon films

Following the growth of the LT films, LEED patterns exhibited attenuated Pt(1 1 1) diffraction spots and a diffuse ring surrounding these spots as has been previously observed [14,15]. This ring corresponds to the lattice constant of ~2.45 Å as for the (0 0 0 1) basal plane of graphite. Formation of the ring instead of the individual spots indicates a high degree of disordering of the graphite single-layer domains, which have various orientations with respect to the Pt(1 1 1) substrate. Some segmentation of this ring was also observed upon higher temperature annealing, indicating a slight preferential alignment of the graphite overlayer with the Pt(1 1 1) surface.

STM images of the LT films revealed wide terraces separated by steps having heights that corresponded to Pt(1 1 1) monoatomic steps underneath the film (Fig. 1a). However, the terrace surface was atomically rough and inhomogeneous, on average. These images exhibited domains where the Moire structure with a periodicity of ~22 Å was clearly observed (Fig. 1b), resulting from a mismatch between the Pt(1 1 1) and graphite(0 0 0 1) hexagonal lattices having unit cell parameters of 2.87 and 2.45 Å, respectively. However, ill-defined structures with high corrugation amplitudes covered most of the surface as shown in Fig. 1c. Tentatively, we have suggested that the carbon surface is represented by small graphite domains and therefore possesses a high density of domain boundaries (see also STM results below for the HT film). This is in agreement with the observation of the graphite-induced diffraction ring rather than spots in LEED and consistent with other studies of this surface where ethylene was used as a precursor [16]. An alternative explanation could be the formation of a second, presumably amorphous, carbon layer since carbon deposition is performed in a very high excess of ethylene. This would be consistent with the high rate of carbon gasification observed on the LT film [17]. Note also, that annealing the surface at 1250 K for 10 min in UHV did not significantly alter the carbon film morphology by STM even though some segmentation of the ring pattern was observed by LEED.

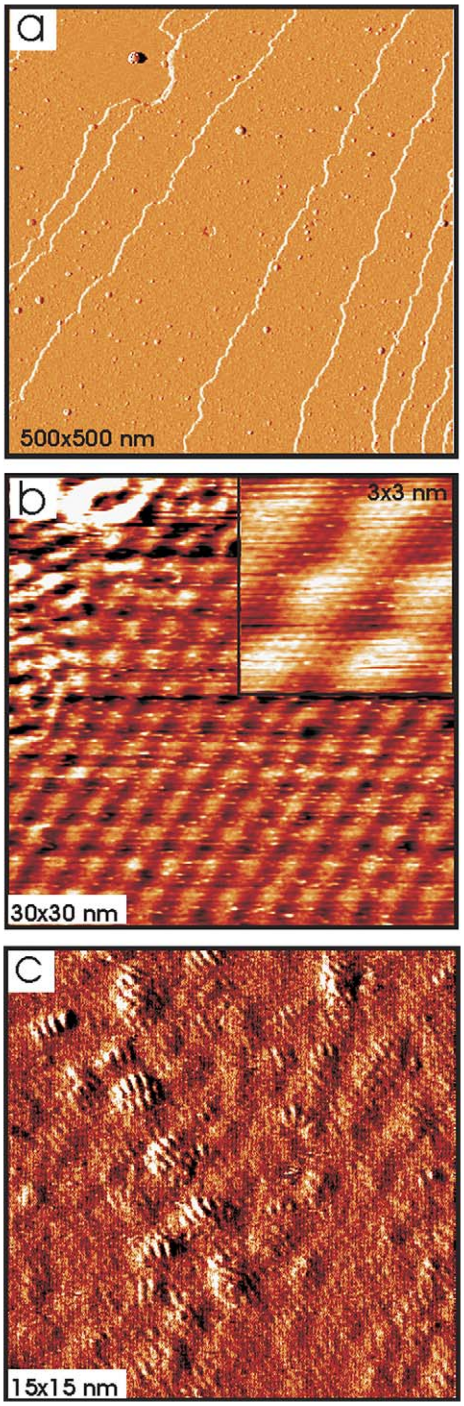

Fig. 1. (a) Large-scale STM image, presented in differentiated contrast, of low temperature carbon films showing flat terraces separated by monatomic steps of a Pt substrate underneath the film. (b and c) STM images of the different areas of the film. Inset in (b) shows atomically resolved Moire structure which arises due to coincidence of hexagonal graphite(0001) and Pt(111) lattices.

LEED patterns of the HT films were different from the LT films showing only the single diffraction ring and no Pt spots. AES spectra did not reveal Pt signals as well. This means that the HT film is thicker than the LT film, and presumably of at least 10–15 Å thickness based on the Auger electron escape depth of Pt [19].

Fig. 2a shows a typical large-scale STM image of the HT film. In contrast to the LT film, a large density of irregularly shaped particles (see inset) is clearly seen. In addition, carbon nanowires up to hundreds of nm in length and 5–10 nm in diameter are formed (see also Fig. 3a).

The terraces consist of graphite domains of various rotational orientations with respect to each other as resolved in Fig. 2b. As a result, numerous domain boundaries are observed. These boundaries may show periodic structures, somewhat resembling the surface of the carbon nanotubes on graphite [20]. The graphitic domains show a hexagonal lattice of protrusions with a ~2.5 Å periodicity similar to the basal plane of HOPG. However, Fig. 2c and d shows that the surface looks different within the same domain: some regions show a honeycomb-like structure (1), similar to HOPG, others – trimer-like (2) structures or “commas” (3). In addition, the star-like feature seen in the middle of Fig. 2d were frequently observed on this sample and may be tentatively assigned to positions where the various rotational orientations of the “trimer” structures meet. It is clear that these effects cannot be assigned to tip asymmetry effects and seem to be electronic in nature possibly resulting from the different stacking of the graphite layers, which are bonded through relatively weak van der Waals forces. Formation of numerous small domains indicates that the surface is highly strained which is quite likely due to the large lattice mismatch (~12%) between graphite(0001) and Pt(111). Therefore, it may well be that the various graphite layers are not in registry, which leads to different incommensurate structures and hence STM images.

Relatively few domains exhibited the Moire structure typically observed for thin graphite films on Pt(111) (see Fig. 2f). Since this superstructure most likely would result from only a single layer of graphite on Pt(111), we conclude that the HT carbon film is relatively thick due to their lack of prominence, which is consistent with the LEED and AES results.

Annealing of the HT film in UHV at 1300 K for 40 min resulted in more frequent observation of nanowires on the surface (cf. Fig. 3a and b). No preferential location of the wires along the step edges is seen, in fact many wires cross multiple steps. The annealed samples also begin to show patches, which are atomically smooth and free of domain boundaries and particles (marked by the star in Fig. 3b). Further annealing causes a significant reduction of the particles’ density and increases the areas of smooth surface, as seen in Fig. 3c. Finally, annealing at 1300 K for 2 h has removed carbon from the surface as revealed both by STM and AES, presumably due to carbon dissolution into the Pt crystal bulk.

Figs. 2a and 3a and c show that carbon nanowires apparently grow from very large particles, the shape of which resemble liquid-like droplets as shown in Fig. 3d and also seen in Fig. 2a. Formation of liquid-like Fe particles during interaction with amorphous carbon at elevated temperatures was previously demonstrated by Zaikovskii et al. using in situ high resolution electron microscopy

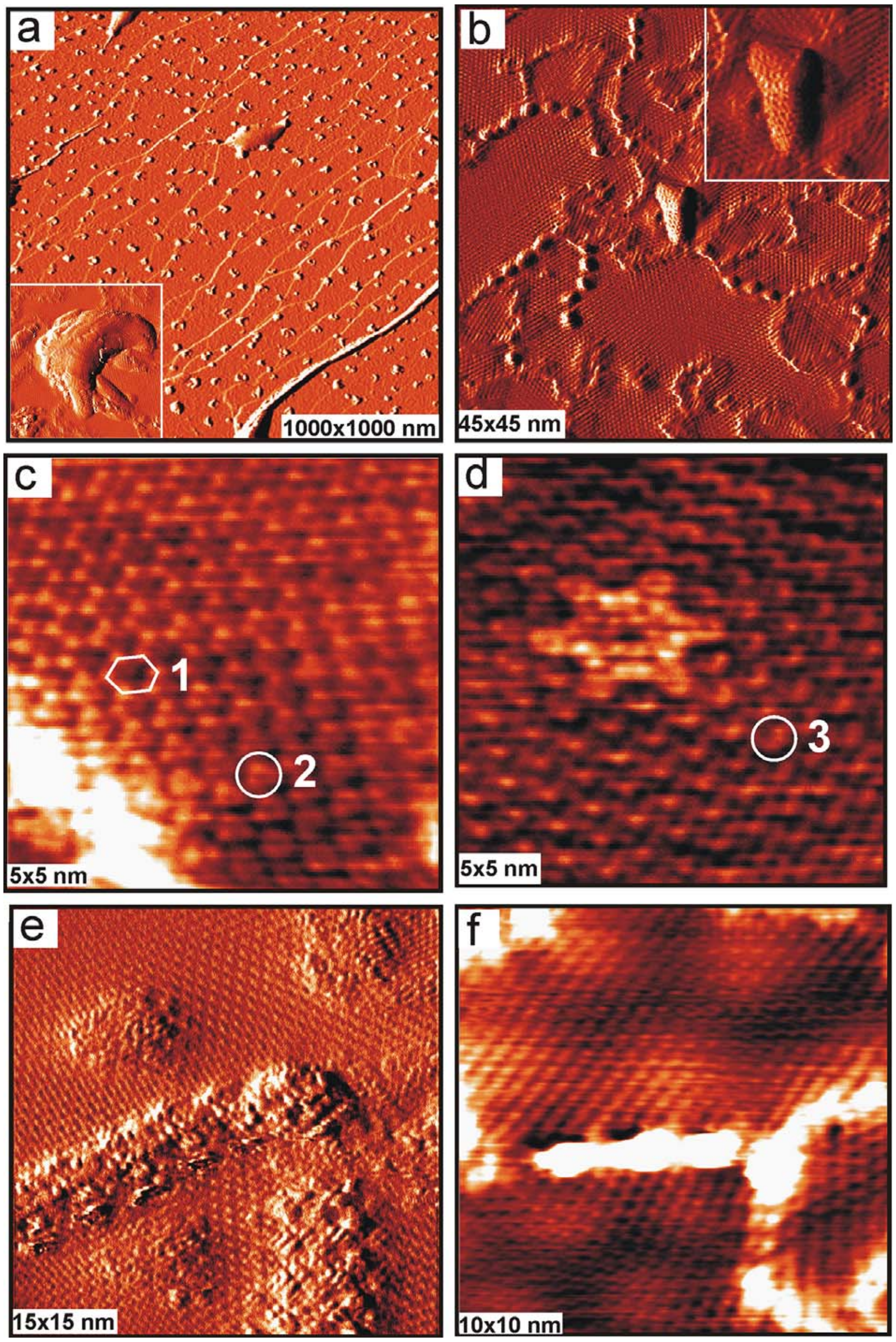

Fig. 2. STM images of the high temperature carbon film (see the text). Inset in (a) shows the close-up of the numerous particles formed on the surface. Inset in (b) zooms in on the particle seen in the middle of the image. In addition to honeycomb structure (1) typical for graphite, the "trimer"- (2) and "comma"-like (3) features are observed. The images (a, b and e) are presented in differentiated contrast.

[21]. Note also, that Fujita et al. [22] has recently reported on the observation of carbon nanowires on a Ni(111) single crystal surface doped with carbon. This finding may be rationalized by the high affinity of 3d-metals for carbon. In fact, the strong carbon–metal interaction lays in the mechanism of the formation of filamentous carbon and carbon nanotubes on Ni, Co and Fe, i.e. metals which readily form metal carbides (see for instance Ref. [23]). However, platinum is known to be very resistant to carbide formation, which is why our observation of carbon nanowires on Pt is very unusual.

Note also that the morphology and AES spectra of the HT carbon film were not affected by exposure to 10^{-6} mbar of O_2 at 1000 K for 15 min, which implies high resistance of the HT films towards gasification. As expected, no hydrogen and CO adsorption above 100 K has been detected by TPD for all films studied. Also water desorbs from these films only in a single peak at ~170 K, which implies forma-

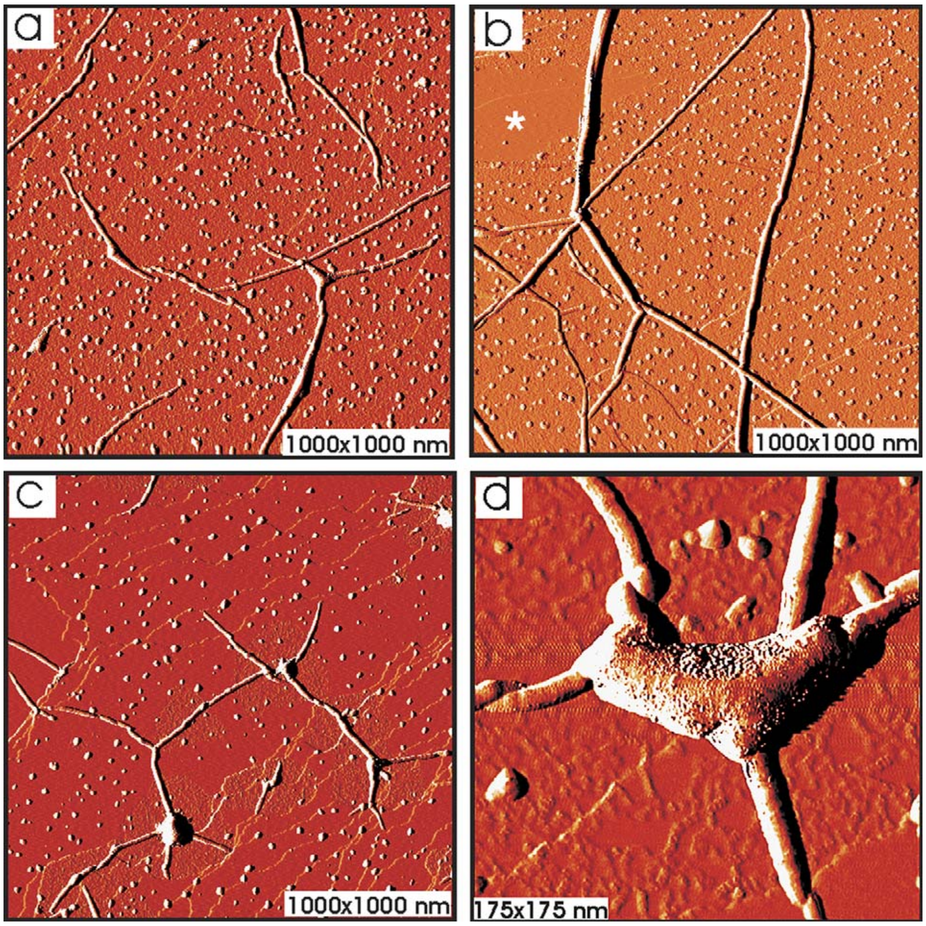

Fig. 3. STM images, presented in differentiated contrast, of the high temperature carbon film upon high temperature annealing in vacuum at 1300 K for 40 min (b) and 80 min (c) (see the text). A large particle resembling a liquid-like feature is zoomed in (c). The star marks the atomically smooth surface (free of domain boundaries and particles), which increases in area upon prolonged annealing in vacuum.

tion of a physisorbed multilayer water film and no water dissociation. Therefore, the TPD results indicate that the carbon surface is essentially inert, even though the films contain a large number of defects as revealed by STM.

3.2. XPS characterization of the carbon films

As prepared, the carbon films exhibit C 1s binding energies (BE) of 284.2 and 284.7 eV for the LT and HT films, respectively, indicating different natures of the carbon formed. This is consistent with the STM results, presented above, showing a different morphology of the carbon overlayers. In order to monitor changes occurring while the film transforms from the LT film into the HT state, we have performed the following experiment. The carbon film, prepared at 1000 K, was further heated in 10^{-7} mbar of ethylene at the specified temperature and cooled down to 1000 K in ethylene ambient, the spectra were then recorded at 1000 K in vacuum. Fig. 4 shows a series of C 1s XPS spectra for different treatment temperatures. It is clearly seen that the carbon peak gains intensity by a factor of two, which is consistent with the increasing thickness of the HT film as implied by AES and LEED (see Section 3.1). In addition, the BE starts to shift to higher energies by ca. 0.5 eV above 1250 K (see inset in Fig. 4). It is important to note that in situ XPS measurements during stepwise

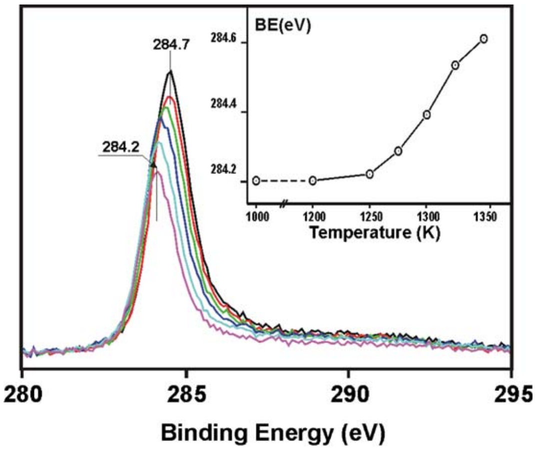

Fig. 4. C 1s region of the XPS spectra of the carbon films after heating of a Pt(111) crystal up to the specified temperature and subsequent cooling in 10^{-7} mbar of ethylene. All spectra were recorded at 1000 K. The inset shows the BE values as a function of the preparation temperature.

heating of the LT film to 1370 K in ethylene ambient did not show any changes in the spectra unless the sample is cooled below 1200 K. This finding strongly suggests that all changes, observed in Fig. 4, develop while the sample is cooling.

In order to rationalize this effect, we have to recall that at elevated temperatures, above ~1200 K, carbon may migrate into the Pt bulk [13]. As a result, the near surface region of the Pt crystal accumulates large quantities of carbon. During the slow cooling cycle this carbon may segregate back to the surface and therefore interact with surface carbon and ethylene to form a thick carbon film. However, it must be the presence of ethylene in an ambient atmosphere during cooling that governs this film formation since prolonged annealing of the HT film at 1300 K in vacuum in fact lead to a gradual disappearance of carbon structures from the surface. Therefore, it is the complex interplay between carbon bulk dissolution, surface segregation and reaction in ethylene ambient that results in a thick carbon film with various forms of carbons present on the surface as observed by STM on the HT films. As clearly seen in Figs. 2 and 3, these carbon structures may exhibit curved surfaces, which can explain the XPS results that the C 1s and Auger C-KLL lines for the HT films resemble rather the spectra of carbon nanotubes and fullerenes than HOPG [17]. Meanwhile, based on XPS results, the LT films are suggested to be pure graphitic in nature.

3.3. Au on the carbon films

Gold, vapor deposited on both the LT and HT films, was examined by STM at 300 K. Various tunneling parameters were used bearing in mind possible tip induced effects frequently observed for gold/graphite systems [9]. However, no small particles that could be unambiguously assigned to Au, were observed on the surface even when Au deposition was performed at 120 K. Domain boundaries, terrace steps, carbon particles and nanowires, which might nucleate Au particles, looked very similar to those prior to gold deposition measured at the same tunneling conditions. Only a few but very large (above 10 nm in size), well shaped particles (and therefore assigned to the Au particles) on both the HT and LT carbon supports have been observed as shown in Fig. 5a and b. This is in contrast to our previous results of Au deposited on oxide films (Al_2O_3, FeO, Fe_3O_4) where small particles, randomly distributed on the support, were observed by STM [6,7]. Therefore, the present STM data indicate that the interac-

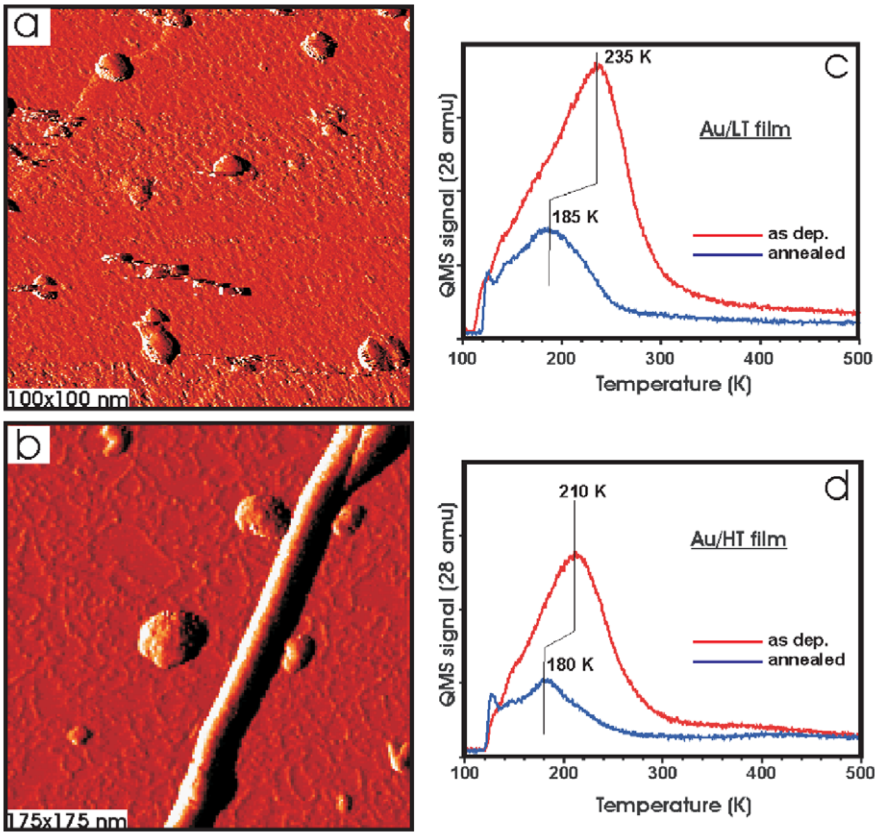

Fig. 5. STM images, presented in differentiated contrast, of gold deposited at 120 K and annealed to 500 K on LT (a) and HT (b) carbon films. The images are recorded at high tunneling bias and low current (3 V, 0.1 nA) in order to avoid tip induced displacement of the particles, however, traces of such movement are seen in (a). Large hexagonally shaped particles are formed as indicated by the arrows in (b). The other particles in this image are similar to those observed on the pristine carbon films with irregular shapes and therefore assigned to carbon (see Fig. 2). The TPD spectra for gold on the LT (c) and HT (d) films are shown for as deposited at 120 K gold and those annealed to 500 K during the first CO TPD run.

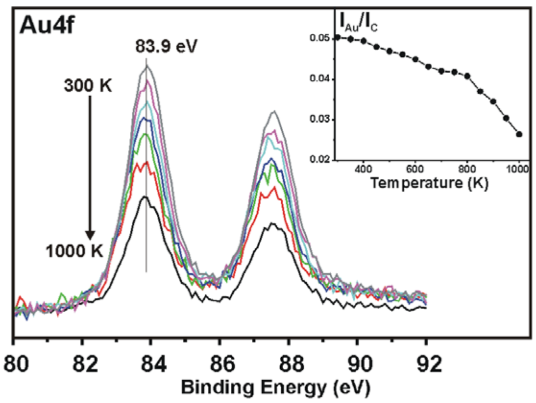

Fig. 6. In situ Au 4f spectra obtained for Au deposited on the HT film upon stepwise heating in vacuum from 300 to 1000 K. Inset shows the intensity ratio of Au 4f and C 1s signals as a function of the annealing temperature.

tion of gold with the carbon supports is weaker than with the oxide surfaces, and that this interaction is not affected by the nature of the carbon support (LT vs HT film).

Fig. 5c and d presents CO TPD spectra for the two Au/C surfaces. These spectra are very similar to those we have observed for Au particles on oxide films [6,7]. As deposited at 120 K Au species adsorb CO much stronger than do annealed Au particles ($T_{des} \sim 235$ K vs ~185 K). In addition, the CO adsorption capacity drops upon annealing. Both observations indicate the adsorption of CO takes place only on low-coordinated Au surface atoms, which decrease in number upon heating and concurrent sintering. In summary, these results fully support our previous conclusions that CO adsorption on gold is essentially independent on the nature of support used, however, the support may influence the stability of the smallest Au species, which in turn depends on the Au/support interaction [3].

XPS measurements were also conducted for ~0.05 ML of gold deposited at 300 K. The Au $4f_{7/2}$ BE value of 84.0 eV indicates that the gold species are essentially in a metallic state and seem to form relatively large particles at 300 K, otherwise one would expect higher BE values as previously observed for very small gold particles [24–27]. Stepwise (50 K step) annealing for 30 min at the temperatures specified in Fig. 6 results only in a strong decrease of the Au 4f signal intensity and not of C 1s. Since gold does not desorb at these temperatures, it seems possible that the Au migrates into the film through the numerous defects present on the film as has been previously observed for small metal particles deposited on thin alumina films [28]. An alternative explanation could be the further sintering of gold at elevated temperatures.

4. Summary

Carbon films were grown on a Pt(1 1 1) single crystal by ethylene ($>10^{-7}$ mbar) decomposition at 1000–1300 K. LEED, AES, XPS and STM studies show that, depending on the preparation conditions, different types of carbon could be formed. In the low temperature regime (~1000 K), the thin carbon film is graphitic in nature. At higher temperatures, thicker carbon films, exposing carbon nanowires and curved graphitic layers, are observed. We suggest that the structure of the carbon film on Pt is the result of the complex interplay of carbon dissolution/segregation and therefore may depend on other parameters such as heating/cooling rates as well. The difference in the structures of the LT and HT film may explain the different reactivity towards oxygen as previously observed [17].

The carbon films exhibited a surface with a high density of defects, however, gold species vapor deposited on these films are found to interact only weakly with the carbon film supports such that only relatively large ~10 nm particles were observed by STM at room temperature. This is in contrast to Au deposited on various oxide films under the same conditions, where much smaller particles were stable upon heating to 500 K. Therefore, the STM data indicate a weak interaction of metallic gold with carbon substrates, independent of the nature and defect structure of the carbon.

Our TPD studies showed that the CO adsorption behavior (desorption temperature, adsorption capacity) is very similar to that observed for various gold/oxide systems studied in our group. These results fully support the conclusion [6,7] that CO adsorption on gold is essentially independent on the nature of support used, however, the support may influence stability of the smallest Au species towards sintering.

Acknowledgments

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