Control over Nanopits on the Basal Plane of Graphite by Remote Argon Plasma and Subsequent Thermal Oxidation

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Control over Nanopits on the Basal Plane of Graphite by Remote Argon Plasma and Subsequent Thermal Oxidation

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The thermal oxidation of the basal plane of highly oriented pyrolytic graphite (HOPG) leads to the formation of shallow circular pits,[1,2] which start to grow from natural defects in the graphite lattice. Recent scanning tunneling microscopy (STM) studies revealed a number of details on the origin of the etch pit formation .[3-8] The etch pits are a single monolayer (335 pm) deep, and the lateral size distribution is often singular, indicating that no spontaneous nucleation occurs. The pit diameter can be controlled by the oxidation time, and pits with diameters as small as a few nanometers can be observed at early stages of the oxidation. Many interesting applications of etch pits have been proposed, e.g., as markers, as calibrators for the z-axis of the STM, as molecular containers, as specific sites for nucleation and chemical or electrochemical reactions, and for immobilization of molecules for STM imaging on an atomically flat HOPG surface. Recently the influence of the etch pits on the formation of ordered structures within a monolayer of molecules adsorbed at the graphite-liquid interface has been investigated.[9,10]

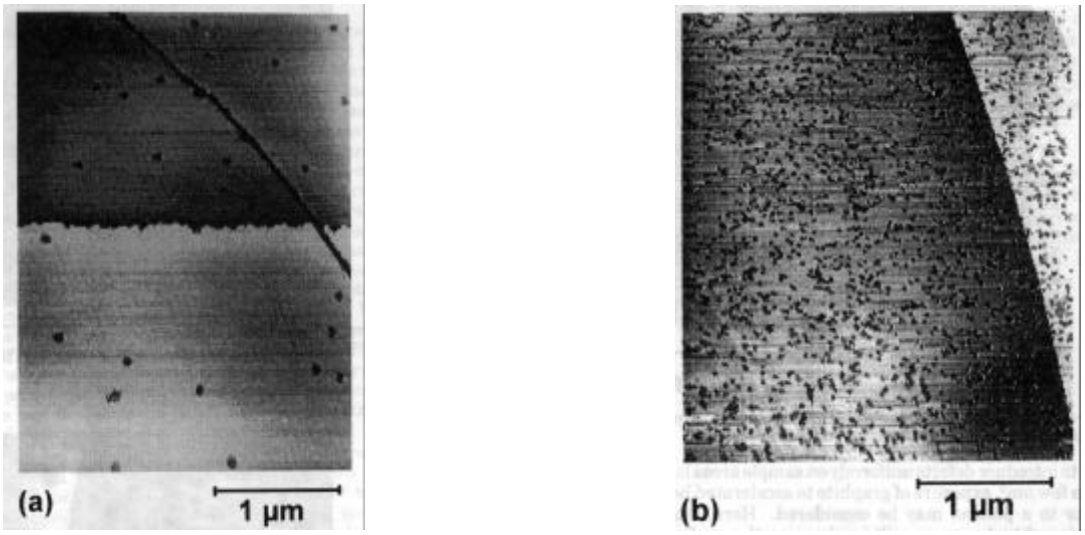

Figure 1. STM images of HOPG thermally oxidized in air at 670 °C (a) without prior plasma treatment and thermal oxidation for 2.5 min and (b) with prior remote argon plasma treatment for 30 s and subsequent thermal oxidation for 1.5 min. The crossing lines are due to monolayer steps and a grain boundary.

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For any of these applications the independent control over pit shape, size distribution, pit size, and pit density is desirable. The *pit shape* can be influenced by temperature, pressure, and medium used for oxidation .[3-5] In many cases the *size distribution* is singular, and therefore the pit size can be controlled by the heating time.[1-8] However, the problem of controlling the *pit density* with a homogeneous size distribution has not been solved satisfactory. Graphite surfaces with pit densities from 1 up to 13 per μm^2 have been prepared,[2-7] but the results are difficult to reproduce, because the density of natural defects varies from sample to sample.[3,7] One method for changing the pit density is based on the effect of consecutive heating-cooling cycles, but a given pit density and size distribution cannot be readily reproduced.[3] Another method may be an O_3-O_2 treatment at elevated temperatures,[5] but a controlled fabrication of different pit densities and sizes has not been reported yet.

Since the pit growth starts exclusively from defects of the graphite lattice within one monolayer, we considered to control the pit density by controlling the density of defects in the first monolayer of graphite. One way to introduce defects is to operate the STM with bias-voltage pulses in situ in various ambients.[11-14] However, if one wants to cover large areas, this method has its limits. In order to introduce defects uniformly on sample areas larger than a few μm^2, exposure of graphite to accelerated heavy ions or to a plasma may be considered. Here, ions or particles of high energy will impinge on the surface of graphite and cause local perturbations or defects in the topmost layer. Subsequent thermal oxidation should lead to the

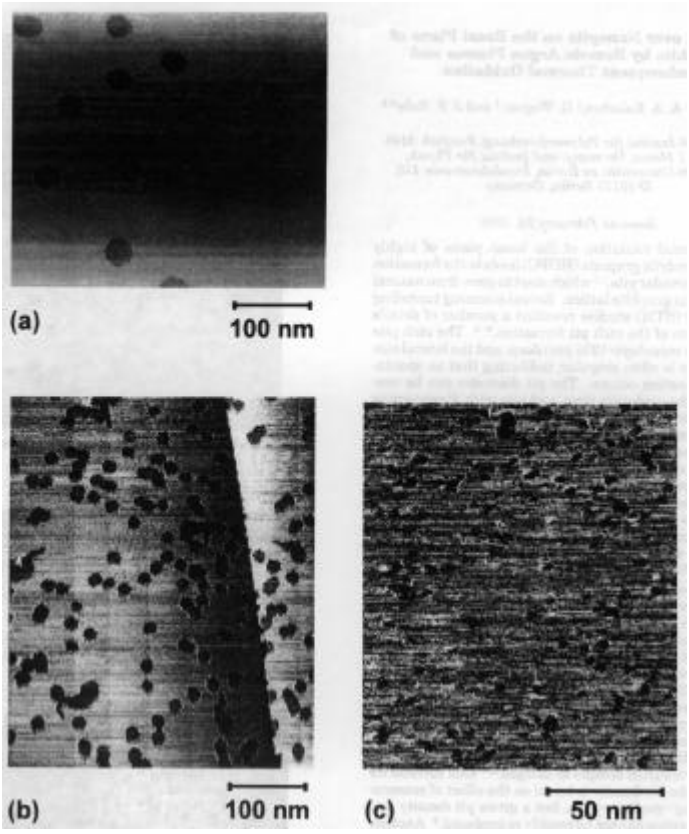

Figure2. STM images of HOPG, treated in remote argon plasma for (a) 10, (b) 30, and (c) 70 s, and subsequently oxidized in air at 670 °C for (a) 90, (b) 90, and (c) 60 s.

development of pits from induced defects. It has been shown that after bombardment with different heavy ions, the location of ion collisions with the graphite surface can be imaged by STM as hillocks ranging from 1 nm to a few nm in diameter.[15-17] The sizes of the affected sites are dependent on the mass of the ions and their energy, and there is a correlation between the ion flux and the surface density of the hillocks. After treatment with radio-frequency oxygen or

argon plasma, the roughness of the graphite surface increases with increasing discharge power.[18-20] So far, however, only surfaces have been studied, which had suffered rather severe destruction, while the early stages of plasma interaction with the basal plane of graphite have not been investigated. In the following we will show that, using sufficiently mild plasma conditions, it is possible to induce atomic scale defects limited to the very first monolayer of graphite and that together with a subsequent thermal oxidation step HOPG samples with a controlled density of monolayer etch pits can be fabricated. HOPG (qualities ZYB and ZYH) was obtained from Advanced Ceramics, Cleveland, USA. Plasma treatment was provided using a LE-301 plasma reactor (Leybold AG), designed for radio-frequency (rf) discharges (13.56 MHz), with an additional attachment for microwave (MW) plasmas (2.45 GHz). The absolute pressure and massflow rate have been measured with a MKS Baratron absolute pressure gauge and massflow controllers with accuracies of 0.005 mbar an 2 mL/min, respectively. All plasma treatments were carried out at a pressure of 0.01 mbar and a massflow rate of 40 mL/min, using argon as a plasma forming gas and operating in the MW-remote plasma mode. The oxidation was performed in a quartz chamber[7] within a few minutes after plasma treatment, with intermediate exposure of the treated graphite to the air. All oxidation experiments took place in air at 670 °C. STM images were obtained with a home-built instrument.[21] Tunneling tips were electrochemically etched (2 N KOH + 6 N NaCN) from a 0.25 nm Pt/Ir (80:20) wire. The images were obtained in constant current mode under ambient conditions. The tip bias was +0.3 V and the current was 2 nA. The images are presented as obtained without any image processing.

HOPG was exposed to remote MW plasma for relatively short times (5-90 s). STM investigations on a scale of several 100 nm did not show the characteristic etch pits, which, however, could be readily observed after subsequent thermal oxidation of the pre-treated samples. The pit density was considerably increased as compared to samples, which were not plasma treated but thermally oxidized directly after cleaving (Figure 1). At given MW-plasma conditions the pit density could be controlled by the time of plasma treatment (Figure 2). While the density of natural defects for different HOPG samples was on the order of 3 μm^{-2}, it was possible to obtain pit densities on the order of 2000 μm^{-2} at a plasma treatment time of 70 s. It should be emphasized that, while the natural pit density varies from sample to sample, the plasma induced pit density depended only on the plasma conditions, provided the number of natural defects is small compared to the number of plasma-induced defects.

Figure 2 shows also that pits are uniform in size, which means that they started to grow simultaneously from statistically distributed defects, and no new defects were created during thermal oxidation. This indicates instantaneous nucleation and growth, as analyzed previously.[8] For a given density of pits, their diameter increases with oxidation time. Therefore, the pit size can be controlled independently from the pit density by the time of thermal oxidation. The average distance between the pits can be varied from about 10 nm (see Figure 2c) up to several 100 nm (Figure la). However, in order to obtain pits of a given diameter for samples with different pit densities, one must consider the influence of the pit density on the growth rate of the pits.[1,7] Therefore, thermal oxidation at given temperature and time for samples with lower and higher pit density results in pits with bigger and smaller diameters, respectively (see parts a and b of Figure 2). Noteworthy, the pits were exactly one monolayer deep, which proves that under the given plasma conditions the plasma modification of the HOPG surface was restricted to the first monolayer only.

In summary, it has been shown that a remote microwave argon plasma can be used in order to introduce point defects on the originally perfect basal plane of highly oriented pyrolytic graphite. By subsequent thermal oxidation these defects can be developed into circular pits, which are a single monolayer deep. This combination of methods allows the monolayer pit density to vary over about 3 orders of magnitude. Independently the pit diameter can be controlled on length scales between a few nanometers up to several 100 nm. The obtained surfaces are expected to play an important role as substrates for the adsorption to nanostructured surfaces.

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(1) Yang, R. T.; Wong, Ch. *J. Chem. Phys*. **1981**, *75*, 4471.

(2) Wong, Ch.; Yang, R. T.; Halpern, B. L. *J. Chem. Phys*. **1982**, *78*, 3325.

(3) Chang, H; Bard, A. *J. Am. Chem. Soc*. **1990**, *112*, 4598; **1991**, *113*,5588.

(4) Chu, X.; Schmidt, L. *Surf. Sci*. **1992**, *268*, 325; *Ind. Eng. Chem. Res*. **1993**, *32*, 1359.

(5) Chu, X.; Schmidt, L. D.; Chen, S. G.; Yang, R. T. *J. Catal*. **1993**, *140*,543.

(6) Morozov, V. N.; Sherman, J.; Kallenbach, N. R.; Du, Shou Ming; Seeman, N. C. *J. Microsc. (Oxford)* **1993**, *170*, 237.

(7) Tracz, A.; Wegner, G.; Rabe, J. P. *Langmuir* **1993**, *9*, 3033.

(8) Pakula, T.; Tracz, A.; Wegner, G.; Rabe, J. P. *J. Chem. Phys*. **1993**, *99*, 8162.

(9) Tracz, A.; Kalachev, A. A.; Wegner, G.; Rabe, J. P. *Verhandl. DPG (VI)* **1994**, *29*, 1629.

(10) Patrick, D. L.; Cee, V. J.; Beebe, T. P., Jr. *Science* **1994**, *265*, 231.

(11) Albrecht, T. R.; Dovek, M. M.; Kirk, M. D.; Lang, C. A.; Quate, C. F.; Smith, D. P. E. *Appl. Phys. Lett*. **1989**, *55*, 23.

(12) Rabe, J. P.; Buchholz, S.; Ritcey, A. M. *J. Vac. Sci. Technol. A* **1990**, *8*, 669.

(13) Terashima, K; Kondoh, M.; Yoshida, T. *J. Vac. Sci. Technol. A* **1990**, *8*, 581.

(14) Buchholz, S.; Fuchs, H.; Rabe, J. P. *Adv. Mater*. **1991**, *3*, 51.

(15) Porte, L.; de Villeneuve, C. H.; Phaner, M. *J. Vac. Sci. Technol. B* **1991**, *9*, 1064-1067.

(16) Shen, T. C; Brockenbrough, R. T.; Hubacek, J. S.; Tucker, J. R.; Lyding, J. W. *J. Vac. Sci. Technol. B* **1991**, *9*, 1376.

(17) Annis, B. K; Pedraza, D. F.; Withrow, S. P. *J. Mater. Res*. **1993**, *8*,2587.

(18) You, H. X.; Brown, N. M. D.; Al-Assadi, K. F.; Meenan, B. J. *J. Mater. Sci. Lett*. **1993**, *12*, 201.

(19) You, H. X.; Brown, N. M. D.; Al-Assadi, K. F. *J. Mater. Sci. Lett*. **1992**, *11*, 21671.

(20) Eklund, E. A.; Snyder, E. J.; Williarns, R. S. *Surf. Sci.* **1993**, *285*, 157.

(21) Rabe, J. P.; Sano, M.; Batchelder, D.; Kalachev, A. A. *J.Microsc. (Oxford)* **1988**, *152*, 573.