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LETTER TO THE EDITOR

The observation of a deuterium isotope effect in controlled line and symbol formation on graphite using a scanning tunnelling microscope

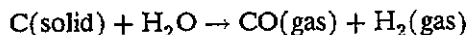
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Abstract. The scanning tunnelling microscope may be utilized to etch well defined lines in highly oriented pyrolytic graphite when operated at ambient conditions. Here we have investigated the role of surface water in this chemical reaction. In the presence of $^1\text{H}_2\text{O}$ surface features have been produced by moving the tip biased at ± 3.5 V at a tip velocity of 10 nm s^{-1} . However, the replacement of the $^1\text{H}_2\text{O}$ with $^2\text{H}_2\text{O}$ in this surface-modifying process causes the threshold voltage to be reduced to ± 3.1 V at the same tip velocity. This observation suggests that no proton transfer occurs in the rate-controlling step.

Recently we have demonstrated the ability of the scanning tunnelling microscope (STM) to etch lines and symbols reproducibly on highly oriented pyrolytic graphite (HOPG) when operated under ambient conditions [1]. This lithographic technique involves moving the tip, biased at or above a certain threshold voltage, over the HOPG surface at a set velocity [1] and is known to be dependent on the presence of a surface coating of water [2]. It is thought to involve the following chemical reactions [3]:



or



Here we present our results on the replacement of the $^1\text{H}_2\text{O}$ with $^2\text{H}_2\text{O}$ in this reaction and note that in the presence of deuterium oxide, the threshold voltage for this surface-modifying process is consistently reduced.

A VG STM 2000 (VG Microtech, Uckfield, UK) with a mechanically cut platinum/iridium (80:20) tip was used throughout this study. The HOPG (ZYA grade; Union Carbide Corporation, OH, USA) was prepared by cleaving the graphite surface layers with adhesive tape. The $^1\text{H}_2\text{O}$ was triple-distilled and deionized before use, the $^2\text{H}_2\text{O}$ (99.8 at.% ^2H ; Aldrich, Poole, UK) was used as supplied. To etch a

continuous line, the tip was moved from a known starting position to a pre-determined location at a set velocity and voltage. The fabrication threshold level was defined as the lowest voltage to achieve line formation on the HOPG substrate which could be subsequently observed by the STM [1]. Initially to ensure that the surface was fully hydrated, 30 μl of $^1\text{H}_2\text{O}$ were allowed to dry on the HOPG surface. The STM observed threshold voltage for the etching of the substrate was determined to be ± 3.5 V for a tip velocity of 10 nm s^{-1} . Similar values have been previously observed for the instrument operating under ambient conditions, indicating that a surface layer of water is normally present in the head chamber of the STM [1]. On the introduction of a silica-gel desiccant this etching process was quickly inhibited, affirming the pivotal role of water in this chemical reaction. Following the removal of the silica-gel, the graphite was freshly cleaved and 30 μl of $^2\text{H}_2\text{O}$ was allowed to dry on the HOPG substrate and the instrument head sealed to prevent $^2\text{H}_2\text{O}/^1\text{H}_2\text{O}$ exchange. Under these conditions the threshold voltage was consistently observed to be reduced by 0.4 V to ± 3.1 V for the same tip velocity. Figure 1 shows a $859 \text{ nm} \times 859 \text{ nm}$ image of the $^2\text{H}_2\text{O}$ coated HOPG surface following lithographic etching at 3.2 V. Three boxes of differing dimensions can be clearly seen to have been etched onto the surface of the graphite. The observed linewidth and depth are measured to be 15 nm and 0.7–1.0 nm respectively. The fact that this reduction in the threshold voltage was due to the presence of the deuterium oxide was further confirmed when the $^2\text{H}_2\text{O}$ was exchanged with $^1\text{H}_2\text{O}$ on opening the instrument head to normal atmosphere. As shown in figure 2 this resulted in the threshold voltage for surface fabrication to be raised to 3.7 V.

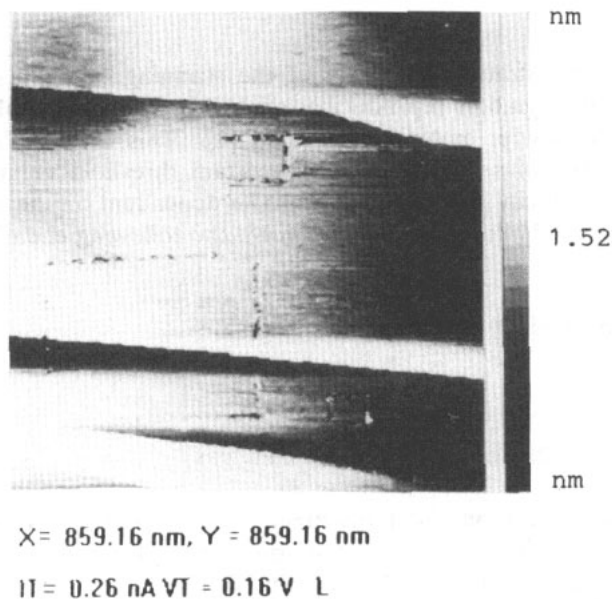


Figure 1. A $859 \text{ nm} \times 859 \text{ nm}$ scan of the $^2\text{H}_2\text{O}$ coated HOPG surface following lithographic etching at 3.2 V. Three boxes have been etched onto the surface; the observed linewidth and depth are 15 nm and 0.7–1.0 nm respectively.

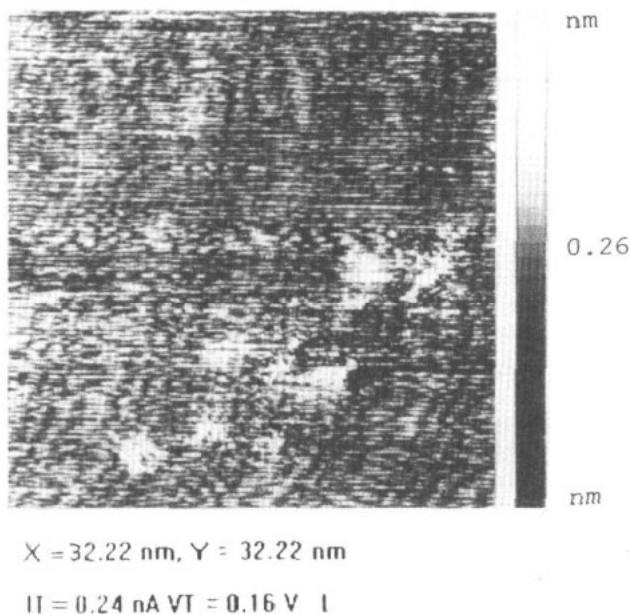


Figure 2. A 32 nm \times 32 nm scan of the HOPG surface following the $^2\text{H}_2\text{O}/^1\text{H}_2\text{O}$ exchange and an attempt to etch a line on the surface using a potential difference of 3.7 V. This etching attempt has resulted in minimal surface damage being observed in the lower right-hand region of the scan, indicating that this is the threshold voltage for the substrate.

Based upon the action of steam on carbon surfaces, many early studies have investigated the chemical reaction of carbon and water [4]. In this study, the reaction was activated by the application of a continuous potential difference. The fact that the etching process was independent of polarity suggests that the reaction is not electrochemical in origin and may be catalysed by a local heating of the graphite surface. Bonds involving deuterium atoms require more energy to break than the hydrogen equivalent units [5]. The finding that the lithographic process for the $^2\text{H}_2\text{O}$ coated surface occurs at 91% of the voltage for a $^1\text{H}_2\text{O}$ coated surface indicates directly that the rate-limiting step for this lithographic reaction requires no transfer of a proton [5].

Through the application of lithographic techniques, this study indicates the unique ability of the STM to distinguish between the presence of $^1\text{H}_2\text{O}$ and $^2\text{H}_2\text{O}$ on the surface of HOPG at the nanometre scale.

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