

# CONTROL OF HYDROGENATION PATTERNING FOR CVD DIAMOND SURFACES BY AFM LOCAL ANODIC OXIDATION

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*Local anodic oxidation (LAO) of hydrogenated CVD diamond surfaces was carefully investigated as a function of the scanning speed, relative humidity and bias voltage. As examples, perfect control of the width of the oxidised lines between 80 and 110 nm was demonstrated for scanning speeds between 20 and 110 nm s<sup>-1</sup>, at 60% relative humidity, and between 45 and 90 nm by switching the humidity from 40% to 60%. The oxidation process is indicated by the decay of the current during the LAO process, which is concluded in about 10 s. The interpretation of the results, which in the literature oscillates between digging grooves and the creation of oxidised bumps, is still quite difficult, since it depends on the AFM mode*

*(‘contact’ or ‘non-contact’) which was used for LAO. A true oxidation process is more likely to occur, as indicated by the present results, and this is in agreement with the presence of oxygen in surface analysis data.* SE/253

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## INTRODUCTION

Several procedures have been proposed in recent years for the modification of surfaces at nanometre and atomic scales using scanning probe microscopy (SPM), in the perspective of applications in fields such as nanoelectronics, nano-optics and nanomechanics.<sup>1–4</sup> Among them, the field enhanced oxidation of silicon,<sup>5,6</sup> GaAs and metal surfaces<sup>7</sup> is arguably one of the most promising approaches. It consists in the application of a small voltage between a positively biased sample, acting as an anode, and a conductive SPM tip brought to the vicinity of the surface, and it causes the formation of a narrow oxide line along the path followed by the scanning tip. The electrochemical process is activated by the intense electric field, which can be in excess of 1 V nm<sup>-1</sup> in this configuration;<sup>8</sup> the phenomenon occurs in ambient air in the presence of a water contamination layer, leading to surface anodisation on a scale depending on the dimensions of the water meniscus formed between the probe and the sample. Using this method, also referred to as local anodic oxidation (LAO), Matsumoto *et al.*<sup>9</sup> succeeded, for example, in operating a single electron transistor at room temperature on a Ti surface.

Pioneering studies in this field were performed by Dagata *et al.*,<sup>10</sup> who demonstrated in 1990 the possibility of patterning hydrogen passivated <111> single crystal silicon by scanning tunnelling microscopy (STM). However, the versatility of atomic force microscopy (AFM) for operating with both conducting and non-conducting samples has prompted its application for the local oxidation of surfaces.<sup>11</sup> Since then, numerous research groups have addressed their attention to the AFM assisted formation of oxidic nanostructures on silicon, both (111) and (100), p-type or n-type doped,<sup>12,13</sup> and a large literature exists today about its mechanism and driving reaction.

More recently, LAO was used for nanoscale modification of the hydrogen terminated diamond surface. With a band gap of about 5.5 eV and an electrical resistivity that can reach 10<sup>15</sup> Ω cm, diamond can reasonably be considered an insulator or a wide band gap semiconductor. However, when its surface is H terminated, the resistivity decreases by several orders of magnitude, even in undoped samples. This phenomenon was observed for the first time in 1989 by Ravi and Landstrass,<sup>14</sup> who noticed a particular type of conductivity due to a highly conductive surface layer: this was true both for monocrystals and polycrystalline samples prepared with by CVD. Hall measurements displayed p-type behaviour of the conductive layer, with a surface hole density of 10<sup>12</sup>–10<sup>13</sup> cm<sup>-2</sup> and a Hall mobility of about 30 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with a maximum value of 70 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Refs. 15, 16). Hydrogen terminates carbon dangling bonds at the surface, creating a situation which is comparable with an ideal, defect free heterointerface. Moreover, owing to the different electronegativities of carbon and hydrogen, the C–H bonds at the surface give rise to a relatively dense dipole layer and, as a consequence, to a negative electron affinity. Maier *et al.*<sup>17</sup> proposed an electrochemical model for diamond surface conductivity, according to which the presence of chemisorbed hydrogen is a condition necessary but not sufficient to explain the p-type layer. The presence of atmospheric species is considered fundamental, and the suggested mechanism is based on the exchange of electrons between the hydrogenated diamond and the atmospheric adsorbates.

On the contrary, an oxygen terminated diamond surface is strongly insulating. In the case of diamond, the oxidation achieved using an SPM is limited to a thin surface layer, and the remaining area is not oxidised, i.e. it remains H terminated. This is a great advantage for nanoscale control of conduction, e.g.