Ni(II) porphine nanolines grown on the Ag(111) surface at room temperature

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Abstract
The room temperature growth and ordering of (porphyrinato)nickel(II) (or nickel(II) porphine, NiP) molecules on the Ag(111) surface have been investigated using scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED). Results obtained at one monolayer (ML) coverage indicate a well-ordered molecular layer in which the porphyrin molecules have a flat orientation with the molecular plane lying parallel to the substrate and forming a hexagonal overlayer on the surface. LEED data obtained from one monolayer of the NiP on the Ag(111) surface show the formation of two mirror domains each rotated either clockwise or counterclockwise by 6° with respect to the substrate. NiP molecules forming a second layer self-assemble at room temperature into well-ordered and uniformly separated nanolines. These nanolines consist of hexagonally ordered NiP molecules and are found to be 1 to 4 molecules wide depending on molecular coverage. The completed second monolayer preserves the same planarity and hexagonal ordering as the first molecular layer but with a 4% lateral relaxation which produces a periodic modulation of approximately 5 nm.

1. Introduction

An important challenge in nanoscience is the ability to control the assembly of functional molecular species into complex supramolecular structures. This controlled assembly of nanostructures offers a number of powerful approaches for the development of molecule-based devices [1, 2]. Due to their interesting physicochemical properties porphyrins are important candidates for use in molecular devices with different functionalities. These flexible molecules with a nearly square planar core conformation are utilized in many technological applications such as molecular optoelectronic gates, molecular wires, light-harvesting arrays for solar energy generation, one-dimensional conductors and semiconductors, oxidation catalysts, sensors, nonlinear optics and nanomaterials [3-7]. In particular, 3d transition metal (TM) porphyrins are widely used in the applications mentioned above, due to their unique electronic structure, which has been the subject of intense experimental and theoretical research during the last decade [8-13].

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An understanding of the porphyrin/inorganic interface with specific electrochemical or photochemical properties is a critical element required for optimizing their use in molecular electronics and in realizing new types of organic molecular devices, especially for photovoltaic applications. Of particular interest are the nature of the bonding between the porphyrin molecules and the surface, as reflected in the electronic charge distribution, and their geometric configuration at the interface. This information is vital for understanding the properties of these organic compounds and their utilization in molecular electronic devices. Recently, a rich variety of molecular nanostructures such as clusters, wires and extended networks have been prepared on different surfaces using porphyrin derivatives and characterized by scanning tunneling microscopy (STM) [13-22]. Porphyrin molecules with extended π-electron systems have found wide use because they tend to bond to surfaces in a flat-lying geometry, which allows functional groups at the molecular periphery to approach each other easily and to engage in bonding interactions. The formation of bonds between complementary molecular components is a widely used approach in the fabrication of nanoscale structures, such as nanomeshes and nanowires, because of their high selectivity, strength and directionality [1, 14, 17].

In the present work using STM and LEED we focus for the first time on the molecular self-assembly of (porphyrinato)nickel(II) (NiP) on the Ag(111) surface in the submonolayer to several monolayers regimes in order to reveal the conformational behaviour of NiP molecules. The results of this work yield important information about the electronic and structural properties of the Ni(II) porphine molecules adsorbed on the Ag(111) surface and show a type of nanoscale templating which could be used for accommodation of guest molecules.

2. Experimental details

The STM experiments were performed at room temperature (RT), using a commercial instrument (Omicron Nanotechnology GmbH), in an ultra-high-vacuum (UHV) system consisting of an analysis chamber (with a base pressure of 2×10^{-11} mbar) and a preparation chamber (8×10^{-11} mbar). An electrochemically etched polycrystalline tungsten tip was used to record STM images in constant current mode. The voltage V_{sample} corresponds to the sample bias with respect to the tip. No drift corrections have been applied to any of the STM images presented in this paper. A single-crystal Ag(111) surface (Surface Preparation Laboratory) was used as a substrate. The Ag(111) crystal was cleaned *in situ* by repeated cycles of argon ion sputtering ($U = 1$ kV) and annealing at 820 K until a LEED pattern with sharp diffraction spots was obtained.

Ni(II) porphine was synthesized according to a published procedure [23]. The NiP was evaporated in a preparation chamber, isolated from the STM chamber, at a rate of about 0.1 ML (monolayer) per minute from a tantalum crucible in a homemade deposition cell operated at a temperature of approximately 600 K. The Ag(111) substrate was maintained at room temperature during NiP deposition. The total pressure during porphyrin deposition was in the 10^{-10} mbar range. Before evaporation the NiP powder was degassed at approximately 500 K for about 10 h to remove water vapour.

3. Results and discussion

Figures 1a and 1b show typical occupied state STM images of a single domain taken from 1 ML of the NiP on the Ag(111) surface. The individual molecules appear as bright protrusions. Ni(II) porphine self-assembles on the Ag(111) surface forming large molecular domains (approximately 100 nm × 100 nm) with a well-defined hexagonal close packed structure as clearly seen in figure 1. In the NiP overlayer each molecule has a flat orientation on the surface with the molecular plane lying parallel to the substrate and surrounded by six neighbouring molecules. The unit cell of the NiP lattice (shown in black in figure 1a) contains a single NiP molecule and has the following parameters: the unit cell vectors are equal to 1.25 ± 0.05 nm, while the angle between them is 120º ± 1º, forming a hexagonal close packed structure. The apparent size of an individual NiP molecule is approximately 1.1 nm. The formation of ordered domains of such extent indicates the presence of a strong intermolecular

interaction, involving the hydrogen atoms of neighbouring NiP molecules, as well as the low diffusion barrier for the molecules on this surface at room temperature. Thus, NiP molecules are physisorbed on the Ag(111) surface and a weak molecule-substrate interaction occurs through the molecular π-electron system.
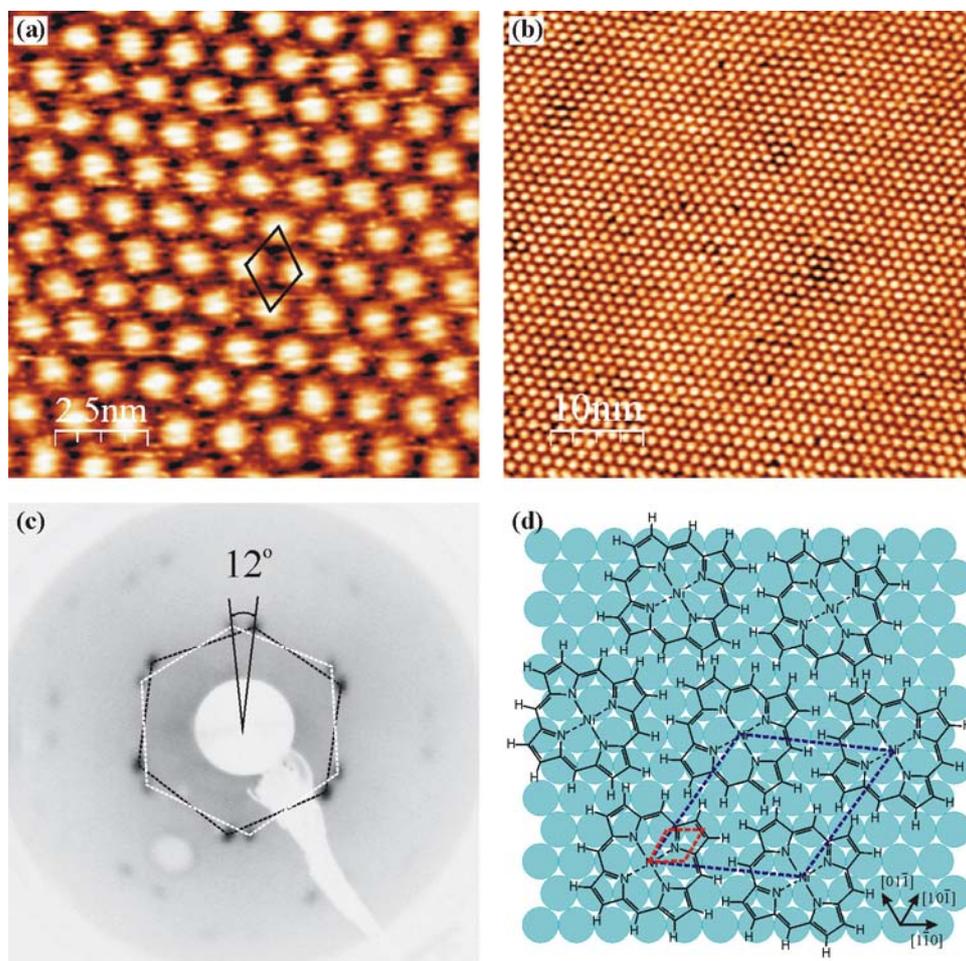
Figure 1. STM images obtained from 1 ML of the NiP on the Ag(111) surface: (a) $I_t = 0.10$ nA, $V_{sample} = -1.20$ V, size 12.5 nm × 12.5 nm and (b) $I_t = 0.20$ nA, $V_{sample} = -1.50$ V, size 50 nm × 50 nm. The unit cell of the NiP overlayer is shown in black. LEED pattern from 1 ML of the NiP on the Ag(111) surface acquired at a primary beam energy of 12 eV (c). The black and white hexagons represent the two NiP domains rotated clockwise and counterclockwise relative to the substrate. Schematic representation of the NiP overlayer (clockwise rotated domain) on the Ag(111) surface (d). The angle between the unit cells of the substrate and the molecular overlayer is equal to 6°.

LEED patterns obtained from 1 ML of the NiP on the Ag(111) surface shows two sets of diffraction spots each forming a hexagonal diffraction pattern (see figure 1c) confirming the structure observed in the STM images. The angle between these two hexagons is equal to 12° ± 1°. Furthermore, these hexagonal patterns obtained from the NiP overlayer are rotated either clockwise or counterclockwise by 6° with respect to the hexagonal pattern formed by diffraction spots from the clean Ag(111) surface. These hexagonal patterns represent two NiP domains which are mirror images of each other, with the mirror plane perpendicular to the substrate and aligned along the close-packed direction of the latter. This results from the lattice mismatch between the substrate and molecular overlayer. Measurements of the lattice constants of the NiP overlayer, determined from a comparative

analysis of LEED images from the overlayer and the substrate, are in agreement with the values obtained by STM. The clarity of the LEED pattern indicates the presence of a highly ordered NiP surface.

The registry of the molecular overlayer with respect to the underlying Ag(111) surface was determined using a combination of the LEED and STM results. Each NiP domain is rotated either clockwise or counterclockwise by 6° with respect to the Ag(111) substrate. Further, the unit cell of the NiP overlayer (1.25 nm) was found to be 9% larger than four times the unit cell length of the substrate (0.289 nm). This mismatch can be accommodated by displacing the position of every second neighbour NiP molecule by one Ag(111) unit cell distance in either the [1-10] direction (clockwise rotated domain) or the [01-1] direction (counterclockwise rotated domain) for every eight unit cell displacements along the [10-1] direction. In this model the resultant angle between the overlayer and substrate unit cells is ± 6°, in agreement with the observed diffraction pattern. Thus, nonchiral NiP molecules self-assemble into two-dimensional chiral domains on the Ag(111) surface. A corresponding model for the NiP molecular overlayer (in the case of the clockwise rotated domain) is shown in figure 1d.

The inter-molecular bonding appears to be stronger than molecule-substrate interaction which is usual for low reactivity substrates such as Ag. This low reactivity of the substrate allows the deposited NiP molecules to be quite mobile. It makes room temperature STM imaging of the molecules difficult at low surface coverage, because individual molecules can be easily moved by the STM tip, confirming that NiP molecules are weakly physisorbed on the Ag(111) surface. Such mobility on the surface and the presence of a strong intermolecular interaction, involving the hydrogen atoms of neighbouring NiP molecules, make the formation of a hexagonal close-packed layer favourable. The lateral intermolecular interactions dominate over site-specific adsorption on the substrate leading to a formation of large well-ordered molecular domains. In turn, a weak interaction between the molecular overlayer and the substrate still leads to azimuthal rotation of the NiP domains with respect to the Ag(111) surface in order to minimize the number of nonequivalent adsorption sites.

Two mirror molecular domains azimuthally rotated with respect to the substrate were previously observed in the case of Ni(II) porphine adsorbed on the Ag passivated Si(111) surface [13], free-base 5,10,15,20-tetrapyridylporphyrin adsorbed on the Ag(111) surface [24] and free-base 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin adsorbed on the Cu(100) surface [25]. For substituted porphyrin molecules the formation of such close-packed domains is mediated by rotation and tilt of the outer substituents attached to the porphyrin macrocycle [24, 25]. The unit cell size and domain symmetry depend strongly on the nature of the substituents. In turn, an azimuthal rotation of a molecular overlayer with respect to the substrate is mediated by molecule-substrate interaction.

At a surface coverage of approximately 1.5 ML Ni(II) porphine molecules self-assemble into nanolines on top of the first molecular overlayer. Figure 2 shows the corresponding STM images where individual molecules forming the first and the second NiP overlayer appear as dark and bright protrusions, respectively. These nanolines are well-ordered and uniformly separated as can be seen from height profiles taken from different regions of the surface, shown in figure 2d. The length of the individual nanolines depends on the Ag(111) terrace size. Lines in excess of 50 nm have been observed. The NiP nanolines are found to be one (figure 2a), two (figure 2b), three and four (figure 2c) molecules wide depending on the total molecular coverage. The wider nanolines consist of hexagonally ordered NiP molecules. Figure 2b shows an example of molecular ordering within a NiP nanoline, which is two molecules wide. The molecules are close-packed and start to form a hexagonal structure with a unit cell parameters approximately equal to corresponding parameters obtained for the first NiP overlayer. In turn, figure 2c shows examples of the wider nanolines oriented along three directions with an angle between them equal to 60° (or 120°). These different branches of nanolines are parallel to the close-packed directions of the first molecular layer following the three-fold symmetry of the latter. The porphyrin molecules in the nanolines forming the second layer have a flat lying orientation on the surface and are situated above the rows formed between NiP molecules in the first molecular layer.
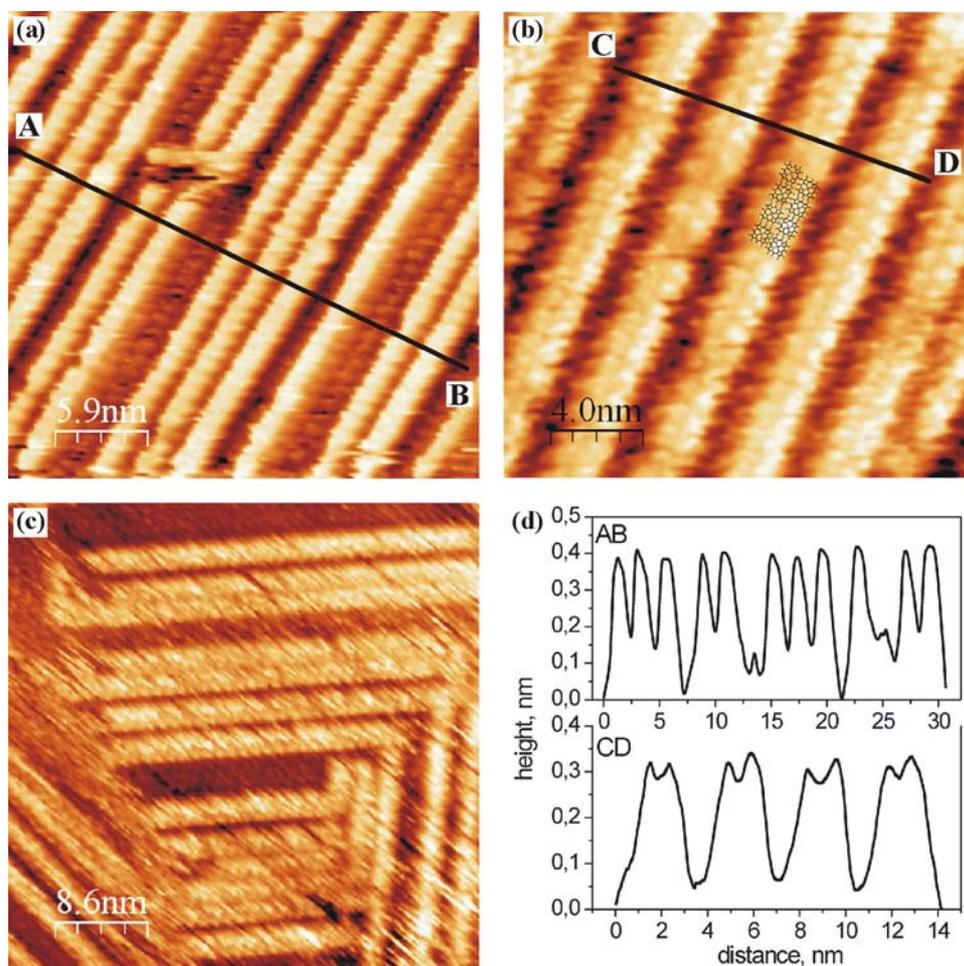
Figure 2. STM images showing ordered NiP nanolines obtained from approximately 1.5 ML of NiP on the Ag(111) surface: (a) I_t = 0.20 nA, V_{sample} = +1.40 V, size 30 nm × 30 nm; (b) I_t = 0.30 nA, V_{sample} = +1.50 V, size 20 nm × 20 nm and (c) I_t = 0.20 nA, V_{sample} = -1.20 V, size 43 nm × 43 nm. (d) Corresponding height profiles indicated by lines on the images (a) and (b).

Similar behaviour was previously observed upon adsorption of free-base 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(4-cyanophenyl)porphyrin on the Au(111) surface studied by low-temperature STM [14]. At submonolayer coverage these molecules form supramolecular wires, which are two molecules wide, due to specific coupling between cyanophenyl substituents mediated by hydrogen bonding. The observed maximum length of these wires was about 100 nm depending on the terrace width on the Au(111) surface, although some branches were also formed due to the three-fold symmetry of the substrate [14].

As the surface coverage is increased to approximately 1.8 ML the NiP nanolines become wider while preserving their parallel ordering (figure 3a). The average width of nanolines is 5.0 ± 0.1 nm. Dark rows approximately 1.2 ± 0.1 nm wide appear between the lines, corresponding to a missing molecular row. Again a hexagonal ordering is observed within these wider nanolines. Figure 3b shows a typical occupied state STM image taken after a further increase in the NiP coverage to approximately 2 ML. It is clearly seen that the second NiP layer preserves the same planarity and hexagonal ordering as the first molecular layer. The lattice constant for the second layer is equal to 1.3 ± 0.05 nm, which is approximately 4% bigger than that of the first layer, indicating a lateral relaxation in the second NiP layer. This relaxation results in a planar distortion of the layer, where some

molecular rows are displaced upwards producing an additional modulation (figure 3b insert), which is clearly observed in STM images recorded at 2ML coverage. This modulation has a periodicity of 5.0 ± 0.1 nm and may be attributed to a filling of the missing molecular rows observed in figure 3a in the transition from 1.8 to 2.0 ML coverage.
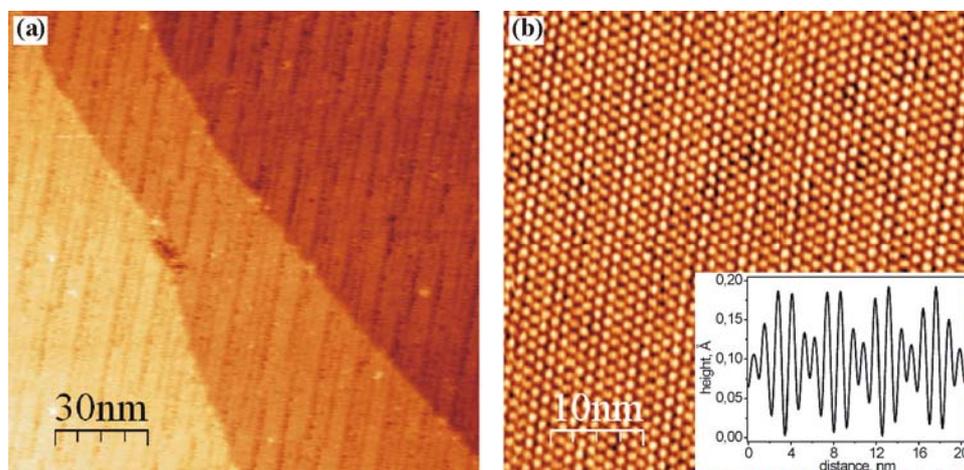
Figure 3. STM image taken from approximately 1.8 ML (a) and 2 ML (b) of the NiP on the Ag(111) surface. (a) I_t = 0.50 nA, V_{sample} = -2.0 V, size 150 nm × 150 nm. (b) I_t = 0.30 nA, V_{sample} = -1.75 V, size 50 nm × 50 nm.

In conclusion, the room temperature growth and ordering of (porphyrinato)nickel(II) on the Ag(111) surface have been investigated using STM and LEED. A well-ordered molecular layer was obtained in which the NiP molecules have a flat orientation with the molecular planes lying parallel to the surface and forming a hexagonal close-packed structure. LEED data obtained from 1 ML of the NiP on the Ag(111) surface show the formation of two hexagonally ordered mirror domains each rotated either clockwise or counterclockwise by 6º with respect to the substrate due to specific intermolecular coupling and a lattice mismatch between the substrate and the molecular overlayer. The lateral intermolecular interactions dominate over site-specific adsorption on the substrate leading to this azimuthal rotation in order to minimize the number of nonequivalent adsorption sites and the local variation in overlayer - substrate distance. NiP molecules forming a second layer self-assemble at room temperature into well-ordered and uniformly separated nanolines. NiP nanolines with length in excess of 50 nm have been observed. These nanolines consist of hexagonally ordered NiP molecules and are found to be 1 to 4 molecules wide depending on molecular coverage. The completed second NiP monolayer preserves the same planarity and hexagonal ordering as the first molecular layer but with a 4% lateral relaxation which produces a periodic modulation of approximately 5 nm.

References
[1]   Barth J V 2007 *Ann. Rev. Phys. Chem.* **58** 375
[2]   Barth J V, Costantini G and Kern K 2005 *Nature* **437** 671
[3]   Chen J, Reed M A, Rawlett A M and Tour J M 1999 *Science* **286** 1550
[4]   Anderson H L 1999 *Chem. Commun.* 2323

[5]   Lin V S Y, DiMagno S G and Therien M J 1994 *Science* **264** 1105
[6]   Tsuda A and Osuka A 2001 *Science* **293** 79
[7]   Senge M O, Fazekas M, Notaras E G A, Blau W J, Zawadzka M, Locos O B and Mhuircheartaigh E M N 2007 *Adv. Mater.* **19** 2737
[8]   Krasnikov S A, Preobrajenski A B, Sergeeva N N, Brzhezinskaya M M, Nesterov M A, Cafolla A A, Senge M O and Vinogradov A S 2007 *Chem. Phys.* **332** 318
[9]   Liao M-S and Scheiner S 2002 *J. Chem. Phys.* **117** 205
[10] de Jong M P, Friedlein R, Sorensen S L, Öhrwall G, Osikowicz W, Tengsted C, Jönsson S K M, Fahlman M and Salaneck W R 2005 *Phys. Rev.* B **72** 035448
[11] Polzonetti G, Carravetta V, Iucci G, Ferri A, Paolucci G, Goldoni A, Parent P, Laffon C and Russo M V 2004 *Chem. Phys.* **296** 87
[12] Krasnikov S A, Sergeeva N N, Brzhezinskaya M M, Preobrajenski A B, Sergeeva Y N, Vinogradov N A, Cafolla A A, Senge M O and Vinogradov A S 2008 *J. Phys.: Condens. Matter* **20** 235207
[13] Beggan J P, Krasnikov S A, Sergeeva N N, Senge M O and Cafolla A A 2008 *J. Phys.: Condens. Matter* **20** 015003
[14] Yokoyama T, Yokoyama S, Kamikado T, Okuno Y and Mashiko S 2001 *Nature* **413** 619
[15] Spillmann H, Kiebele A, Stöhr M, Jung T A, Bonifazi D, Cheng F and Diederich F 2006 *Adv. Mater.* **18** 275
[16] Elemans J A W, van Hameren R, Nolte R J M and Rowan A E 2006 *Adv. Mater.* **18** 1251
[17] Grill L, Dyer M, Lafferentz L, Persson M, Peters M V and Hecht S 2007 *Nat. Nanotechnol.* **2** 687
[18] Nishiyama F, Yokoyama T, Kamikado T, Yokoyama S, Mashiko S, Sakaguchi K and Kikuchi K 2007 *Adv. Mater.* **19** 117
[19] Krasnikov S A, Hanson C J, Brougham D F and Cafolla A A 2007 *J. Phys.: Condens. Matter* **19** 446005
[20] Bonifazi D, Kiebele A, Stöhr M, Cheng F, Jung T, Diederich F and Spillmann H 2007 *Adv. Funct. Mater.* **17** 1051
[21] Li Q, Yamazaki S, Eguchi T, Hasegawa Y, Kim H, Kahng S J, Jia J F and Xue Q K 2008 *Nanotechnology* **19** 465707
[22] Guo X L, Dong Z C, Trifonov A S, Miki K, Mashiko S and Okamoto T 2004 *Nanotechnology* **15** S402
[23] Unger E, Bobinger U, Dreybrodt W and Schweitzer-Stenner R 1993 *J. Phys. Chem.* **97** 9956
[24] Auwärter W, Weber-Bargioni A, Riemann A, Schiffrin A, Gröning O, Fasel R and Barth J V 2006 *J. Chem. Phys.* **124** 194708
[25] Sekiguchi T, Wakayama Y, Yokoyama S, Kamikado T and Mashiko S 2004 *Thin Solid Films* **464-465** 393
[26] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colchero J, Gomez-Herrero J and Baro A M 2007 *Rev. Sci. Instrum.* **78** 013705