Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Development of a Hybrid SNOM/STM and its Application to Organic Ultra-Thin Films

Ken Nakajima [a b], Ruggero Micheletto [a], Keita Mitsui [a], Takashi Isoshima [a b], Masahiko Hara [a b], Tatsuo Wada [a b], Hiroyuki Sasabe [a b] & Wolfgang Knoll [a c]

[a] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama, 351-0198, JAPAN

[b] Core Research for Evolutional Science Technology (CREST), Japan Science and Technology Corporation (JST), 2-1 Hirosawa, Wako, Saitama, 351-0198, JAPAN

[c] Max-Planck-Institute for Polymer Research, Ackermannweg, 10, D-55021, Mainz, GERMANY

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 209–214
Reprints available directly from the publisher
Photocopying permitted by license only

Development of a hybrid SNOM/STM and its application to organic ultra-thin films

KEN NAKAJIMA [a,b], RUGGERO MICHELETTO [a], KEITA MITSUI [a], TAKASHI ISOSHIMA [a,b], MASAHIKO HARA [a,b], TATSUO WADA [a,b], HIROYUKI SASABE [a,b] and WOLFGANG KNOLL [a,c]

[a] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-0198, JAPAN

[b] Core Research for Evolutional Science Technology (CREST), Japan Science and Technology Corporation (JST), 2-1 Hirosawa, Wako, Saitama 351-0198, JAPAN

[c] Max-Planck-Institute for Polymer Research, Ackermannweg, 10, D-55021, Mainz, GERMANY

Received 28 April 1998; accepted 29 April 1998

In order to overcome one of the drawbacks in scanning near-field optical microscopy (SNOM), *i.e.*, a low spatial resolution caused by a rather poor sample-probe distance control, we are designing a hybrid system of SNOM with scanning tunneling microscopy (STM) by introducing a metal-coated optical fiber tip with an apex of a nanometer-scale aperture. We present the recent developments of our homemade hybrid SNOM/STM system.

Keywords: scannning near-field optical microscopy; scanning tunneling microscopy; metal-coated optical fiber tip

INTRODUCTION

Currently, scanning near-field optical microscopy (SNOM) [1,2] has been increasingly drawing our attention. One of the drawbacks in SNOM is a poor sample-probe distance control that is realized by a simple optical feedback or by a shear force system [3]. In the former case, due to the intrinsic nature of the near-field, the probe cannot reach to the close proximity down to nm-scale. In the latter case, the neccesity of the tip vibration results in a low lateral resolution. Thus, these systems are characterized by a low spatial resolution and an unstable distance lock.

To avoid these difficulties and improve the performance of SNOM instrument, we are currently designing a hybrid system of SNOM with

scanning tunneling microscopy (STM) (hybrid SNOM/STM) by introducing a metal-coated optical fiber tip with an apex of a nanometer-scale aperture for simultaneous SNOM/STM imaging. The system can be designed for both "collection mode" to map the optical properties without losing the extremely high resolution of conventional STM technique and "illumination mode" to stimulate the sample with light using such a sharpened probe tip.

According to literature, there have already been several reports which described the combination of SNOM and STM. Kawata *et al.* designed the system where a metallic tip interfered the evanescent field standing on the sample and the scattered light was collected during STM scanning [4]. However, neither "illumination" nor "collection" mode is accessible with this method. On the other hand, a metal-coated optical fiber tip with an aperture can be used for both modes, although several disadvantages have been reported up to now; the large-size top of the fiber tip caused by metallization resulted in a low spatial resolution or the distortion of the obtained image [5].

In order to overcome such difficulties in using a metal-coated optical fiber tip, we employed the new scheme of the tip fabrication which will be described in the experimental section of this paper. Several examples of STM images obtained by using our SNOM/STM system will be also presented.

EXPERIMENTS

SNOM/STM head was designed regarding the compatibility with a commercially available STM instrument, NanoScope II (Digital Instruments, CA, USA). The quality of the head was confirmed by observations in "STM mode" of several samples, using this head combined with a normal Pt-Ir tip.

The fabrication procedure of a metal-coated optical fiber tip is based on the selective chemical etching of optical fibers originally developed by Ohtsu *et al.* [6,7]. 23 mol% GeO_2-doped optical fiber is etched in the two solutions with two different volume ratios of NH_4F : HF : H_2O successively. The scanning electron microscope (SEM) image (S-900, Hitachi, Japan) of the optical fiber tip is shown in Fig. 1(a). The cone angle is about 25°.

Pt ion-coating to the tapered optical fiber was performed in low vacuum chamber (about 0.1 Torr). The thickness of Pt layer was *ca.* 100 nm. The tip is dipped in an acrylic resin solution afterwards. Due to the surface tension of the resin solution, the sub-micrometer top region of the sharpened core is exposed from the resin solution after the withdrawal of the tip from the

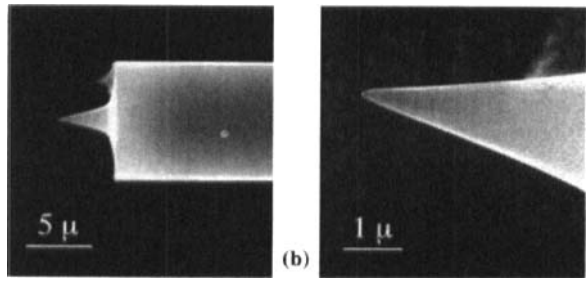

FIGURE 1 SEM images of homemade optical fiber tip. (a) The whole shape of the tip. (b) The tip after forming extremely small aperture (< 100 nm).

solution [7]. The uncovered portion with the resin film is etched in a KI-I_2 solution to form an aperture. Though the shape of the uncovered area depends on several factors such as a cone angle and a withdrawal speed, we obtained extremely small apertures down to a few tens of nanometers with high reproducibility. Fig. 1(b) shows the SEM image of the fiber tip after the formation of the aperture, where the size of the aperture is less than 100 nm and the curvature of the tip is around 30 nm.

The procedure of the tip fabrication can be closed at this stage if the tip is used only for normal SNOM measurements, while the neccesity of simultaneous SNOM/STM imaging imposes one more step; the coating of Pt ultrathin layer. Note that this step is original in our paper. The optimized value of the Pt layer thickness (*ca.* 25 nm) results in the a half-transparent metallic aperture. This 25nm thickness is thick enough to get the electrical connection to the first preamplifier circuit which is attached to the SNOM/STM head.

RESULTS AND DISCUSSION

Quality of Homemade Optical Fiber Tip

The quality of our metal-coated optical fiber tip was examined in combination with NanoScope II STM head. Au (instead of Pt) of *ca.* 100 nm thickness was coated to an optical fiber tip. In Fig. 2, the obtained STM image of a fleshly cleaved highly oriented pyrolytic graphite (HOPG) is shown, where the scan size is 6.5 × 6.5 nm^2, I_t = 4 nA and V_{sample} = 200 mV. As compared with normal STM images of HOPG, there are many streak noises possibly caused by the mechanical instability of the tip. The instability may come from the

dimensions of the tip. As the original diameter of the cladding (125 μm) is much smaller than that of a normal STM tip, its resonant frequency must be considerably decreased, resulting in the streak noises observed in the image.

In spite of the instability, an atomic resolution was achieved in the image. Although the image was attained with the tip which is covered merely by 100 nm Au layer (without any aperture), the electrical connection without the loss of the image quality was not lost even with thickness around 30 nm. Thus we confirmed the sufficient capability of our homemade metal-coated optical fiber tip to investigate nanometric objects in "STM mode."

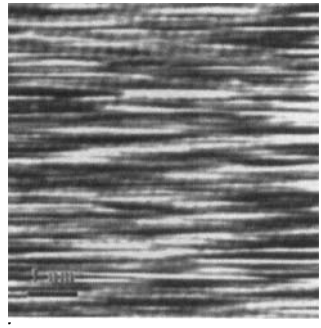

FIGURE 2 The STM image of an HOPG obtained by using NanoScope II STM head with Au-coated optical fiber tip.

Combination of SNOM/STM Head and Optical Fiber Tip

As the example to illustrate the quality of our SNOM/STM head, we made STM imaging of a liquid crystalline "guest-host" system. As well known, 4'-*n*-octyl-4-cyanobiphenyl (8CB) molecule shows the stable anchoring structure with high ordering on molybdenum disulfide (MoS_2) [8]. Moreover, this ordered structure can act as a "host" system [9], where azo dyes such as 1-hydroxy-1'-hexyl-azobenzene (6AZ) can be dispersed as "guest" molecules. In Fig. 3, a typical STM image of 8CB/6AZ (9 : 1) mixture on MoS_2 is shown. The image was taken by using NanoScope II STM head with a Pt-Ir tip. The scan size is 20 × 20 nm^2, I_t = 0.2 nA and V_{sample} = 1.4 V. It was possible to distinguish azobenzene moiety from biphenyl groups on each molecule as indicated by arrows. The material system also draws our attention because it may be possible that *cis-trans* switching phenomenon of an individual 6AZ molecule is observed by exciting it

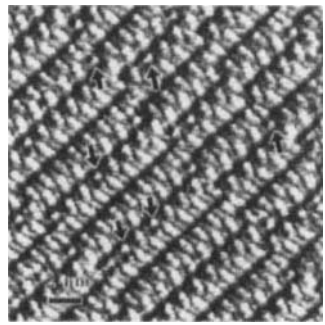

FIGURE 3 The STM image of 8CB/6AZ (9 : 1) mixture on MoS_2 taken by NanoScope II STM head with Pt-Ir tip.

using our developing SNOM/STM optical fiber tip.

A large-scale STM image of 8CB/6AZ (9 : 1) mixture on MoS_2 taken by NanoScope II head with a Pt-Ir tip is shown in Fig. 4(a), where the scan size is 100×100 nm^2, $I_t = 0.3$ nA and $V_{sample} = 1.2$ V. The molecular rows are clearly resolved and there exists a molecule-missing defect at the lower-left part in the image as indicated by an arrow. Bright spots observed randomly and separately in the image represent defects of underlying MoS_2.

As shown in Fig. 4(b), our homemade SNOM/STM head with a Pt-coated optical fiber tip was utilized to observe the same sample. The scan size, I_t and V_{sample} are almost identical to those in Fig. 4(a). While the rows of cyanobiphenyl molecules cannot be imaged in this imaging, specific defect structures of MoS_2 are visible with the same appearance in Fig. 4(a). We should note that similar images to Fig. 4(b) are often observed (even in using a conventional STM instrument) in case that a tip condition is not ideal due to contaminants. However, since a Pt-coated optical fiber tip has the potential to give an atomic-scale resolution as indicated by Fig. 2, we can expect a higher resolution in STM mode with our hybrid SNOM/STM system in the near future.

From a view point of acquisition for optical information in localized area, there will be expected many possible usages of our hybrid SNOM/STM system because the system showed a sufficient resolution down to nanometer-scale in STM mode. We are now establishing an access to individual molecule level which have many interesting features such as photoluminescence and electroluminescence by approaching the optical fiber tip to the close proximity

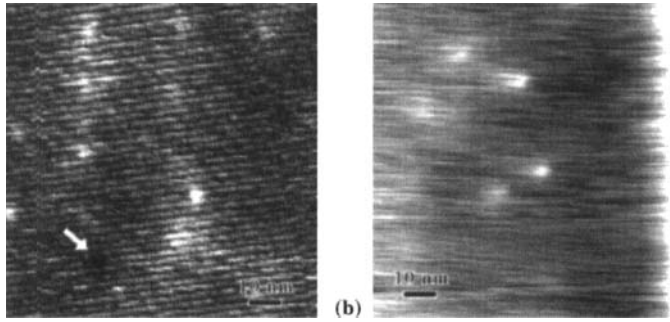

FIGURE 4 Large-scale STM images of 8CB/6AZ (9 : 1) mixture on MoS_2 taken by (a) NanoScope II STM head with Pt-Ir tip and (b) our homemade SNOM/STM head with Pt-coated optical fiber tip.

of the molecules and exciting them by photon and/or electron injection. Such developments are now in progress and will be reported elsewhere.

CONCLUSION

We confirmed the present capability of our developing hybrid SNOM/STM system as a tool to investigate nanoscopic phenomena by showing several examples like HOPG and 8CB/6AZ mixed "guest-host" system on MoS_2. At present, the system showed a sufficient resolution down to nanometer-scale in STM. By solving its mechanical instability and by optimizing the tip fabrication technique, the system can be improved to realize multi-applicability.

Acknowledgements

The authors thank Prof. Ohtsu and Dr. Mononobe of the Kanagawa Academy of Science and Technology (KSP), Japan, for giving useful information of their tip fabrication method. One of the authors (K.N.) has been supported by a grant from Special Postdoctoral Researchers Program, RIKEN, Japan.

References

[1.] D. W. Pohl, W. Denk and M. Lanz, Appl. Phys. Lett., **44**, 651 (1984).
[2.] E. Betzig, M. Issacson and A. Lewis, Appl. Phys. Lett., **51**, 2088 (1987).
[3.] E. Betzig and J. K. Trautman, Science, **257**, 189 (1992).
[4.] Y. Inoue and S. Kawata, J. Microscopy, **14**, 178 (1994).
[5.] K. Lieberman and A. Lewis, Appl. Phys. Lett., **62**, 1335 (1993).
[6.] S. Mononobe, M. Naya, T. Saiki and M. Ohtsu, Appl. Opt., **36**, 1496 (1997).
[7.] T. Pangaribuan, K. Yamada, S. Jiang, H. Ohsawa and M. Ohtsu, Jpn. J. Appl. Phys., **31**, L1302 (1992).
[8.] M. Hara, Y. Iwakabe, K. Tochigi, H. Sasabe, A. F. Garito, A. Yamada, Nature, **344**, 228 (1990).
[9.] Y. Iwakabe, M. Hara, K. Kondo, K. Tochigi, A. Mukoh, A. Yamada, A. F. Garito, H. Sasabe, Jpn. J. Appl. Phys., **30**, 2542 (1991).