NEAR-FIELD ILLUMNINATION METHOD FOR THE SPECTROSCOPIC MEASUREMENT IN EXTENDED-NANO SPACE

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ABSTRACT

To reveal unique liquid properties at interface in nanochannels, a novel illumination method using near-field light, which enable nanoscale spectroscopy in confined nanochannels has been developed for the first time. In this report, the near-field probe integrated in microchip was designed and fabricated. The generation of near-field light which decays in depth direction in confined space was verified. Various spectroscopic measurements using this illumination method will contribute to various researches in nanofluidics by revealing the nanoscale distribution of flow and liquid property.

KEYWORDS: Extended-nano space, Near-field optics, Spectroscopy

INTRODUCTION

Recent progresses in microfluidic researches achieved fluidic systems using 10-1000 nm scale nanochannels, referred to as extended-nano space. Extended-nano space is a transient space from single molecules to the bulk condensed phase, and the fluidics and chemistry in extended-nano space have not been well explored. Our research group have reported many unique properties of liquids, such as higher proton mobility and higher viscosity [1]. To explain these liquid properties, we proposed a proton-transfer phase model, in which water molecules are loosely coupled within a few tens of nanometers from the liquid-solid interface. This model predicts the different liquid property between interface and inside. However, direct measurement of unique properties of liquid at interface in extended-nano space has not been achieved. The difficulty here is spectroscopic measurement in the extended-nano space with 10 nm scale depth resolution, smaller than wavelength of light. One conceivable approach for direct measurement of liquid property at interface in extended-nano space is to illuminate near-interface area in nanochannels with 10–100 nm scale, thinner than proton transfer phase, and to do variable spectroscopic measurements. For example, tracing pH-sensitive fluorescent probe may offer information about proton mobility within illuminated area. In this paper, we developed a novel illumination method to illuminate thin near-interface area in nanochannels with 10–100 nm scale.

THEORY

The concept of this study is shown in Figure.1. According to the proton transfer phase model, in the extended-nano space fabricated in fused silica, water molecules within approximately 50 nm from the liquid-solid interface shows the unique liquid properties (Figure.1a). However, spatial resolution of conventional spectroscopic measurement is limited to approximately 200 nm due to diffraction limit. Near-field spectroscopy, using near-field light generated when nano structures smaller than wavelength are exposed to incident light, can overcome this diffraction limit. This research aims to develop extended-nano near-field spectroscopy, in which interface of nanochannel are illuminated by near-field light, smaller than the scale of proton transfer phase, for the spectroscopic measurement (Figure.1b). The challenge here is the development of near-field probe applicable to confined space smaller than wavelength, because previous near-field spectroscopy uses near-field scanning optical microscope (NSOM), which cannot be applied to confined space.

The basic design of microchip is shown in Figure.1c. Near-field light is generated by nanoslit apertures on a thin metallic film. Because near-field light is generated only in the close vicinity of apertures, apertures should be embedded in immediate proximity to nanochannels. The challenge here is fabrication process to realize this positional relationship.

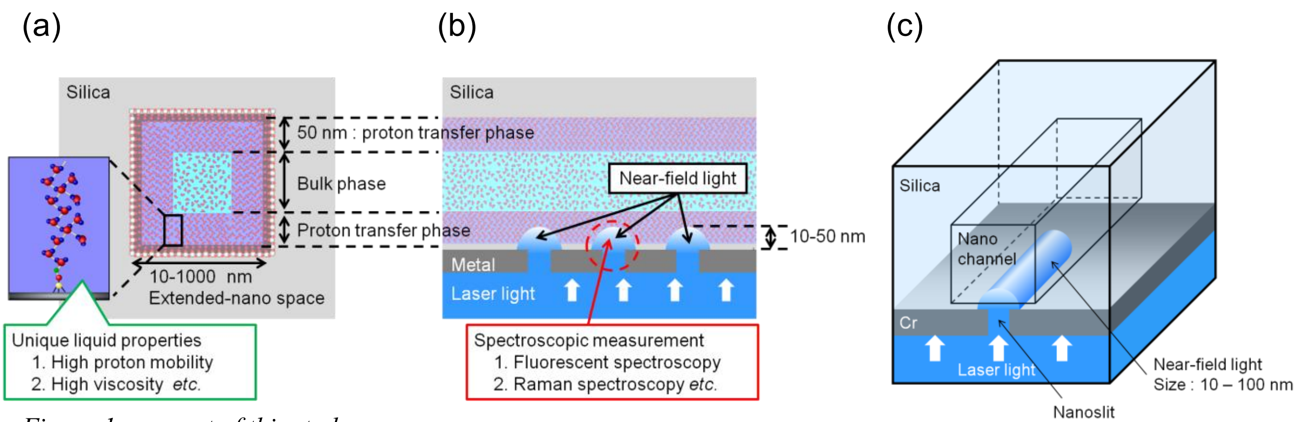

Figure 1: concept of this study
(a) – description of proton transfer phase model
(b) – concept of extended-nano near-field spectroscopy
(c) – basic design of microchip

In our device, slit-shaped apertures are used to improve near-field light intensity, although circle-shaped apertures are used in most aperture-NSOM to obtain high resolution in all directions. According to the numerical simulation of electromagnetic field based on finite-difference-time-domain method, light (wavelength : 488 nm) propagating through circle-shaped aperture (diameter : 50 nm) on a chromium layer (thickness : 150 nm) decays rapidly because no propagation mode exists. Intensity of near-field light is decreased to a few thousandths that of incident light. Moreover, decay length becomes shorter when smaller aperture is used. Low intensity of near-field light, and poor contrast between light from aperture and light penetrating Cr film, suffer sensitive spectroscopy. On the contrary, light with polarization perpendicular to nanoslits propagates through nanoslits no matter how narrow the slit is [2]. According to the numerical simulation under the same condition except the infinitely long slit-shaped aperture (width : 20 nm), near-field light generated by a nanoslit is as intense as incident light.

The size of illuminated area can be adjusted by slit width. To design the slit width, we simulated the light intensity distribution of near-field light under the same condition to the previous simulation, except slit width. Figure. 2 shows the relationship between the distance from chromium layer and light intensity for the variable slit width, 20, 40, 80, 120, 160 nm. To characterize the depth resolution, decay length, the distance for the intensity to decay by a factor of 1/e compared to the intensity at aperture end, was calculated for each slit width (Table. 1). Depth resolution as small as slit width were expected. For the spectroscopy of proton transfer phase, nanoslit narrower than 40 nm is favorable.

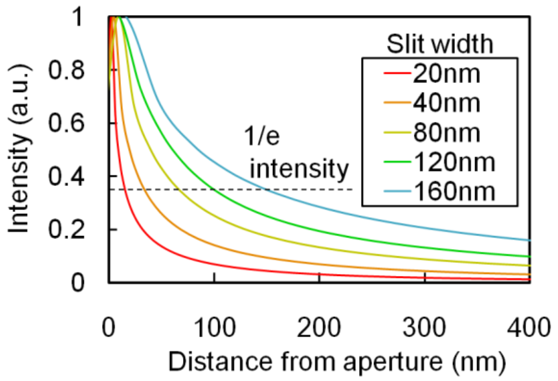

Figure 2: Intensity distribution of near-field light generated by nanoslits with different width

Table 1:decay length of light intensity distribution

Slit width (nm)	20	40	80	120	160
1/e decay length (nm)	14	36	72	110	144

EXPERIMENTAL

Fabrication of microchip

Microchip was fabricated as follows (Figure. 3a). Microchannels and nanochannels were fabricated on plane silica substrates using photolithography and dry etching. Depth of nanochannels was various, although width of nanochannels was fixed to 500 µm. One of substrates was sputtered with chromium with 150 nm thickness. Then, nanoslit apertures were fabricated on chromium layer with focused ion beam so that nanoslit were on nanochannels. Length of nanoslits was 3.5 µm. Width of nanoslits was 40 nm or 120 nm. To confirm that surface property of nanochannel is the same to that of silica, the chromium layer was coated with sputtered silica, whose thickness was 5 nm. One substrate was bonded to another silica substrate under 2 MPa pressure and 250 ℃ temperature after O_2/CF_4 plasma treatment. The detail of low temperature bonding technology is described in [3]. Picture of the microchip was shown in Figure. 3b. Pressure capacity of channels was more than 300 kPa, enough for various experiments using extended-nano fluidic system.

Verification of near-field light generation in closed channel

It is difficult to directly measure the light intensity distribution in confined space using NSOM. To verify the near-field light generation in confined channel, fluorescence excitation in nanochannel was analyzed.

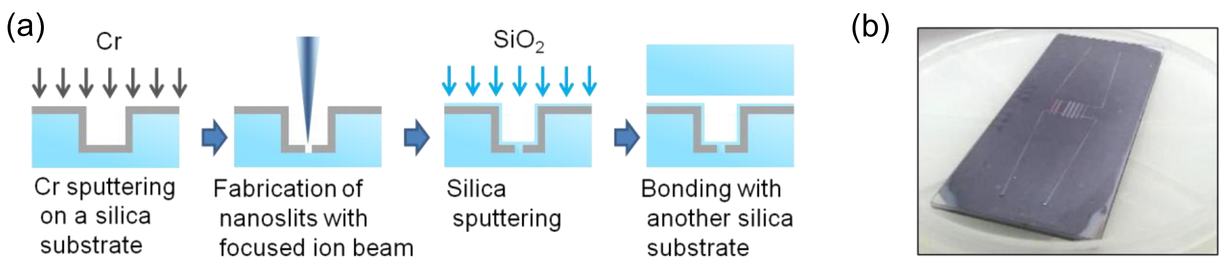

Figure 3: fabrication of microchip
(a) – fabrication process
(b) – picture of a fabricated microchip

Experimental setup is shown in Figure. 4. Fluorescent solution (0.1 mM Alexa Fluor 488, 10 mM KCl) was introduced in nanochannels. Then, nanoslits on nanochannels were illuminated with a 488-nm laser. The intensity of fluorescence generated where near-field light and nanochannels overlapped were measured with fluorescent microscope. Ideally, signal intensity of bright spot should be proportional to the integral of light intensity distribution over the nanochannel. Thus, we calculated the "expected" relationship between channel depth and fluorescent intensity by integrating simulated light intensity distribution in depth direction

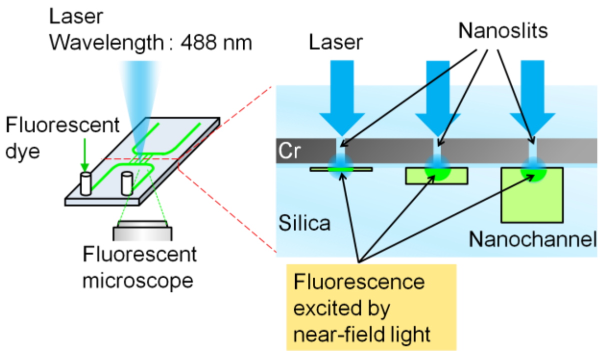

Figure 4: setup for the verification of near-field light generation in closed channel

RESULTS AND DISCUSSION

Relationship between channel depth and fluorescent intensity on 120-nm-width nanoslits was shown in Figure. 5. Measured values showed good agreement with simulated value, indicating the generation of near-field light which decays in depth direction in confined space. However, fluorescent intensity on 40-nm-width nanoslits was quite-variable among slits. This is partially due to low processing accuracy of narrow nanoslits. Near-field light generation including excitation of localized surface plasmon polaritons is sensitive to the processing accuracy of nanoslits. Improving processing accuracy can enable spectroscopic measurements with 10 nm scale spatial resolution.

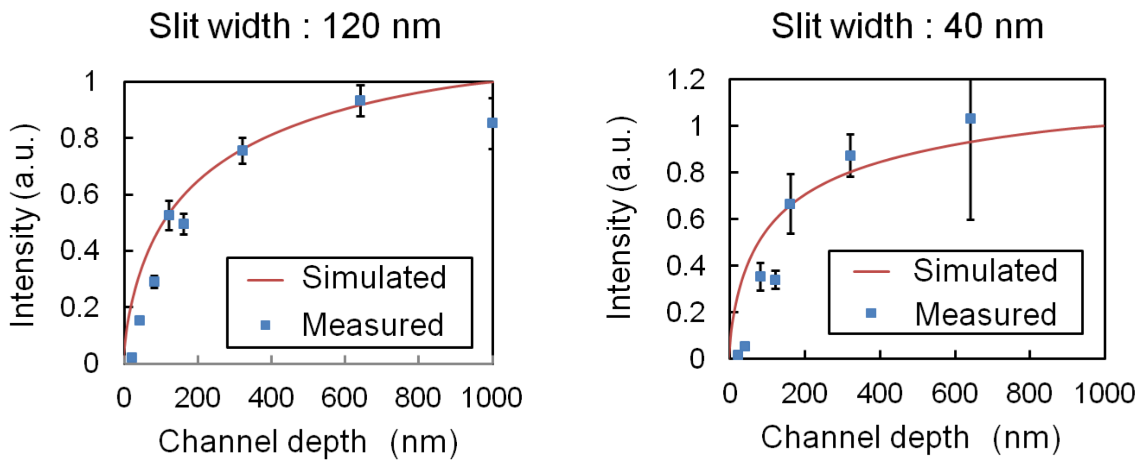

Figure 5: relationship between channel depth and fluorescent intensity excited by near-field light

CONCLUSION

We developed a novel illumination method using near-field light applicable to confined channels. The generation of near-field light which decays in depth direction in confined space was achived for the first time. Although some difficulties about the processing accuracy are remaining to achieve 10 nm scale spatial resolution, spectroscopic measurements using this illumination method will contribute to various researches in nanofluidics by revealing the nanoscale distribution of flow and liquid property.

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