Measurement of the temperature distribution of resistively heated nanowires using CdSe/ZnS nanocrystals

Peter Löw*, Nobuyuki Takama*, Beomjoon Kim* and Christian Bergaud**

INTRODUCTION

Temperature has a significant impact on the kinetics of biomolecules, e.g. proteins and DNA. In order to study these temperature dependent phenomena, temperature control must be precise and quickly adjustable. One way to satisfy these requirements is to use temperature jump techniques such as pulsed laser systems which locally increase the temperature of a liquid containing the molecule to be studied\(^1\). The response time of such a system can be very fast, with time constants of down to 50 picoseconds\(^2\).

In our research, we aim to develop a heating device which can easily be integrated into Lab-on-a-chip systems. By using resistive heating in a metal or semiconductor circuit, on-chip temperature can be controlled. However, compared to laser pulse systems, this kind of approach is typically associated with relatively slow response times. In order to optimize response times of a resistive heater, it is necessary to decrease its thermal mass and consequently its size. It is also necessary to minimize the dissipation of heat from the heating element so that the introduced amount of heat can be kept local and at a minimum. Miniaturization of resistive heating devices for the purpose of fast response has earlier been described by Arata et al\(^3\).

To further improve response times, we propose to use nanowires as heating elements. Nanowires are interesting in that their size and composition can be precisely controlled when fabricated via VLS growth\(^4\) or nanoporous membrane templates\(^5\). Precise control like this opens up possibilities to fine-tune the properties of a nanowire heater, for example in terms of temperature distribution. Combined with the sensing capabilities of semiconductor nanowires\(^6\), nanowire heating will represent a valuable tool for on-chip molecule studies.

The focus of this paper lies on the characterization of static temperature in resistively heated metal nanowires.

In order to characterize temperature changes on a submicron scale, classical methods like IR thermal imaging do not provide the necessary spatial resolution\(^7\)\(^8\). Other methods have been developed for this purpose, e.g. Raman spectroscopy\(^9\) and Scanning Thermal Microscopy\(^10\). These methods, on the other hand, typically show low performance in terms of temporal resolution and are also rather expensive. To allow for both high spatial and temporal resolution, we have investigated the use of temperature dependent fluorescent probes to characterize sub-micron temperature changes. Other papers have presented similar techniques with various fluorescent particles\(^11\)\(^12\). We focus here on the case of CdSe/ZnS nanocrystals, which fluorescence has been shown to depend on temperature\(^13\).

EXPERIMENTAL

Nanowire fabrication

Electron Beam Lithography (EBL) was used to realize nanowires as described in the following. ZEP520-A7 resist (Zeon corp.) was first spincoated onto a thermally oxidized silicon substrate at 5000 rpm. Structures were written directly in the resist at a dose of 120 \(\mu\)C/cm\(^2\). After development, evaporation of a 35 nm thick Nickel layer was performed. ZDMAC solution (Zeon Corp.) maintained at 60 °C was finally used to realize a lift-off.
The resulting nanowires were 20–40 μm long and 200–500 nm wide. The nanowires were finally passivated with a 100 nm thick SiO₂ layer using sputtering.

**Carboxyl functionalized CdSe/ZnS core-shell nanocrystals** with emission peak at 655 nm were purchased from Quantum Dot Corp. The diameter of these particles was around 10 nm and the particle concentration of the original nanocrystal solution was 8.2 μM. The solution was diluted by 1:100 in a 25 mM MES buffer of pH 5.0 before usage.

A simple deposition and drying technique was used to place the nanocrystals on top of the nanowire samples. To allow for a uniform distribution after drying of the nanocrystal solution, a glass coverslip was placed above the sample surface, creating a gap of height about 100 μm. The nanocrystal solution was then introduced into the gap by capillary forces and left to dry (Figure 2). A dense and uniform layer of nanocrystals was achieved.

**Temperature measurement**

The temperature dependence of the nanocrystal layer was calibrated by externally heating the sample using a microscope heating stage. Fluorescence intensities of the CdSe/ZnS nanocrystals were captured at temperatures between 30 °C and 60 °C with intervals of 5 °C. A calibration curve of the temperature dependence could thereby be obtained (Figure 3). All measurements were done in ambient air.

Resistive heating was achieved by applying a DC current through a nanowire at an ambient temperature of 30 °C. For fluorescence observation during temperature measurement, a BX-51 fluorescence microscope from Olympus with appropriate filter sets was used. Fluorescent images were captured, recorded and analyzed on a computer using a Cascade II: 512 CCD camera from Photometrics in combination with MetaMorph software from Molecular Devices Corp.

**RESULTS**

Figure 4 shows the nanocrystal fluorescence on the nanowire when no current was applied. The fluorescence intensity is higher on the metal parts, e.g. the nanowire, than on the SiO₂ due to differences in reflectance. The intensity along the unheated nanowire, from one end to the other, is shown as a blue curve in Figure 6. As can be seen, the initial intensity distribution, when no current was applied and when the temperature was all over the same, had a lower value in the middle than at the ends.

Figure 5 shows the case when a current of 2.5 mA was applied through the nanowire, equaling a power of approximately 6 mW. A local increase in temperature.
The decrease in intensity on the nanowire is clearly seen. The intensity along the heated nanowire is shown as a red curve in Figure 6. The intensity decrease indicates that the temperature was increased. The relative decrease was slightly larger in the middle than at the ends.

Using the calibration data in Figure 3, the intensity change, i.e. the difference between the blue and the red curve of Figure 6, was converted to temperature (Figure 7). The result suggests a temperature between 55 °C and 65 °C along the nanowire and that the central part is hotter than the ends.

**CONCLUSIONS & FUTURE WORK**

Characterization of nanowire temperature using CdSe/ZnS nanocrystal fluorescence was investigated.

The technique showed promise in enabling measurement of temperature distribution on a microscale. Further enhancement of the nanocrystal stability may improve the resolution. Future studies will aim to investigate alternative fluorescent particles for temperature measurement. Particles of interest are rare-earth nanocrystals as well as classical molecular dyes such as Rhodamine B. The main purpose of pursuing measurement by fluorescent thermometry is to enable simultaneous measurement of temperature distribution and high-speed temperature changes. Our experiments were performed in dry conditions, i.e. in ambient air. For the purpose of nanowire heating in biological applications, it will be necessary to perform temperature measurements in wet conditions as well, considering that this is the natural environment of biomolecules. Furthermore, the current nanowire system is rather power inefficient due to large heat dissipation into the silicon substrate underneath. This will be improved by performing a back-etch of the sample in order to obtain a suspended nanowire structure.

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