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研究課題名（和文）High Q-factor ultra-thin Si nano-resonators for ultra-sensitive gas-sensing applications

研究課題名（英文）High Q-factor ultra-thin Si nano-resonators for ultra-sensitive gas-sensing applications

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研究成果の概要（和文）：ナノソネーターは、高感度センサーとして機能する小さな機械である。高感度を実現するためには、ナノレゾネーターを極限まで薄くすることが有効である。しかし、大量かつ安価に製造するには多くの課題がある。我々は、既存のSiナノレゾネータを超薄型化することで改良し、その挙動を研究することを提案した。
我々は、極薄シリコンナノレゾネーター（幅～10nm、長さ～100ミクロン）の作製法の開発に成功した。その特性を実験的、理論的に研究した。特に、共振周波数とQ値に焦点を当てて研究を行った。その結果、高い周波数可変性、高いQ値、そしてCO2ガスの検出が可能となった。

研究成果の学術的意義や社会的意義
Nanotechnology can help us build a technologically improved society, for example, by making efficient devices like nanoresonators that are ultrasensitive, small, cheap, and energy efficient. We improved Si nanoresonators so they can be more sensitive, versatile, and easy to make in large numbers.

研究成果の概要（英文）：Nanoresonator are vibrating nano-mechanical structures that can work as ultrasensitive gas sensors for novel applications in healthcare, environmental, industrial monitoring, etc. Smaller mass and higher Q-factor generally enhances the performance of nanoresonator-based sensors. In this research we have developed ultrathin Si nanoresonators for gas sensing applications.
We developed a scalable fabrication process to make ~10 nm wide, ~100 micron long ultrathin Si nanoresonator. We achieved remarkable electrostatic tunability in resonance frequency and nonlinearity comparable to atomically-thin resonators. We theoretically and experimentally studied the Q-factor reduction phenomena in nanoscale and identified a cause and potential ways to enhance it. Finally, we conducted high sensitivity CO2 gas sensing experiments with our Si nanoresonators. In summary, we successfully developed scalable, tunable, high Q-factor, ultrathin Si nanoresonators for gas-sensing.

研究分野：Nano / micro electromechanical systems

キーワード：Nanoresonator　NEMS　Si microfabrication　frequency tuning　Q-factor　gas sensing　EBL　DRIE

１．研究開始当初の背景

Nanoresonators are devices that contain a nanometer-size, vibrating mechanical structure. The 'nanomechanical' structure is like a tiny spring (k) – mass (m) system capable of undergoing resonant vibration at a frequency, $f_0 = (1/2\pi)\sqrt{k/m}$. The resonant vibration of the nanomechanical structure is being used for developing a series of novel practical applications, such as, ultrasensitive mass, force, charge, biomolecule sensing, high-frequency signal processing, logic and information processing, quantum computation, etc. For a concrete example, consider adding a minuscule mass ($\Delta m \ll m$) to (the already quite small mass of) the vibrating nanomechanical structure, such as by adsorption of gas molecules on the resonator's surface; this can induce a measurable shift in the resonance frequency (Δf_0) for detecting and measuring Δm. This can provide a way for creating ultrasensitive gas sensors for new applications in healthcare (such as early detection of metabolic diseases), environmental / industrial monitoring, etc. Reducing the nanoresonator's initial mass (m) is an effective way to improve the sensitivity and resolution in gas-sensing and other applications. Therefore, attempts are being made for making nanoresonators using atomically thin materials, such as, graphene. Such atomically thin resonators also provide wide electrostatic tunability of resonance frequency, where resonance frequency can be tuned by simply adjusting a voltage applied at a nearby electrode. Unfortunately, atomically thin resonators also require unconventional fabrication methods, and they lack large-scale single-crystal-quality base materials. In addition, room temperature quality factor in atomically thin resonators is often significantly deteriorated by increased surface loss and the stress-dominated resonance frequencies are usually less predictable. On the other hand, making nanoresonators by downsizing conventional silicon (Si) resonators offers the benefits of high-quality, affordable, wafer-scale material, and an established, scalable, monolithic fabrication process, and potentially higher quality-factors; however, conventional Si resonators are relatively thicker and lack in room-temperature electrostatic tunability. In this research, our goal is to develop ultrathin (~ 10 nm) Si nanoresonators in an attempt to bridge the gap between scalable fabrication and potentially higher Q-factor in one hand (Si) with small-mass and tunability in the other hand (atomically thin resonators). Thus, the fundamental research question we asked at the beginning of this research is whether ultra-thin (~ 10 nm) Si resonators can show high mass-sensitivity and predictable, stable, high-Q dynamics. The research that followed over the next three years has attempted to answer this question with both experimental and theoretical investigations, as we discuss in the following sections.

２．研究の目的

The research undertaken by this project can be divided into the following goals. First, to develop a device fabrication process to create ultrathin Si nano-resonators with widths of the order of a few tens of nanometers (nm). The desired process should be a scalable, top-down fabrication process which can monolithically create all device components in parallel. Then, to develop a method by which the fabricated nanoresonators can be characterized especially to investigate their resonance characteristics and Q-factor, theoretically understand the underlying mechanisms, and achieve specific goals by design optimization. Next, to study the electrical/ mechanical/ electromechanical behavior of Si in ~ 10 nm length-scale. Finally, build a set up to study gas-sensing experiments and employ them in targeted sensing of specific gases (CO_2, NH_3, Acetone, etc.)

３．研究の方法

The basic ultra-thin Si nanoresonator device structure we aim to develop is shown in Fig. 1a. The devices include a nanometer-scale, suspended, straight (with rectangular cross-section) mechanical beam (nano-resonator) of width (t) ~ 10 nm, length (t) ~ 100 μm, height (w) ~ 10 nm, with two in-plane (side-gate), parallelly situated electrodes (at ~ 2 μm distance, g_0) for electrostatically actuating mechanical vibration in the nanoresonator and capacitively detecting the resulting motion. Thus, all basic components required for the functioning of the device are built right into the chip. To build many of these devices and all of their components in parallel from a single piece of material (wafer), we developed a fabrication process using conventional Si microfabrication tools available in our cleanroom. Starting from a commercial (IceMos technology Ltd., UK) silicon-on-insulator (SOI) wafer with ~ 7.5 μm thick, n-type (resistivity ~ 0.002 Ω.cm), single-crystal (100) Si device layer (box SiO2 layer is ~ 2.2 μm thick and the handle layer Si is ~ 508 μm), the devices are fabricated by photolithography, electron-beam lithography, deep-reactive-ion-etching (DRIE) of the Si device layer, and vapor HF etching of the box-layer SiO_2 for suspending the nanoresonators, as shown in Fig. 1b.

The resonance characteristics of the fabricated nanoresonator devices are characterized inside vacuum

chambers (10^{-1} – 10^{-4} Pa) (Fig. 1c-d) at either room temperature (300 K) or at low temperature (down to about 100 K). A dc voltage (V_{dc}) is applied on the nanoresonator and an ac voltage ($\tilde{V}_{ac} = V_{ac} \cos 2\pi f\tau$) of amplitude V_{ac} that varies sinusoidally with time (τ) at frequency, f, is applied at the electrostatic actuation electrode. This creates a periodic driving force at frequency f on the nanoresonator resulting in a periodic displacement (vibration), which is detected by measuring the electrical signal generated at the detection electrode (due to capacitance variation) by passing it through a transimpedance amplifier (TIA) (Fig. 1c) and then to a lock-in detection system (MFLI, Zurich Instruments, Switzerland). For gas sensing experiments, a dedicated vacuum chamber is custom-built, where various gases can be introduced into the chamber where the resonator is set to vibrate (Fig. 1d). The resonance frequency shifts are detected using the same detection strategy illustrated above. Further details on device fabrication and device characterization methods can be found in an article (especially in the 'supporting information' document) we published on this research available at Nano Letters **23**, 11517–11525 (2023).

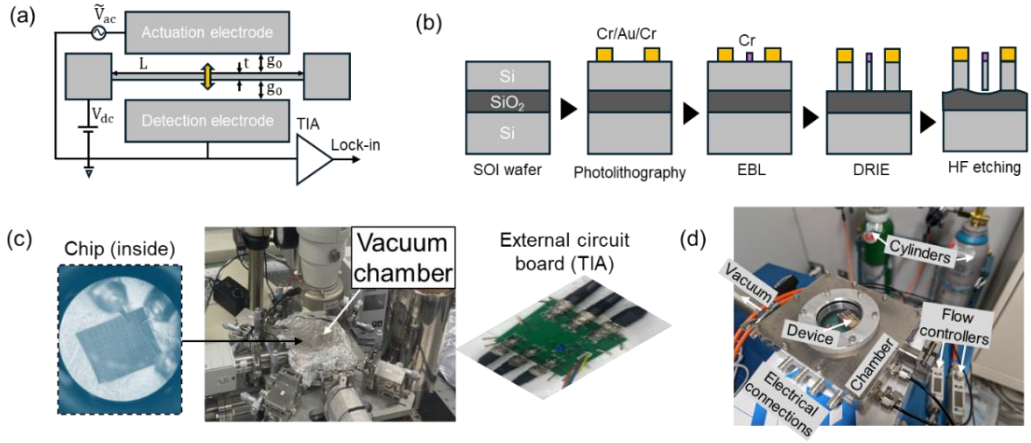


Fig. 1: Schematic illustration of (a) the proposed ultra-thin Si nanoresonator devices with integrated on-chip actuation and sensing mechanisms, (b) device fabrication process developed for the fabrication of the proposed ultra-thin Si nanoresonator devices; photographs of (c) the device characterization setup, (d) gas-sensing setup.

4．研究成果

4.1 Results of device fabrication

Developing a fabrication process for the proposed ultra-thin Si nanoresonator devices is the first and foremost challenge to overcome for achieving the goals of this research. The primary challenge in this step lies in the unusually high aspect ratio of the desired suspended nanomechanical structures, which demands precise patterning and Si etching process. Using the fabrication route described above (Fig. 1b), we successfully developed Si nanoresonators having t in the range of 20 – 300 nm, L in the range of 100 – 300 µm, w ~ 7.5 µm, g_0 ~ 2 µm. The highest aspect ratios in the thinnest Si nanoresonators, $L{:}\,t \approx 10^4{:}\,1$ and $w{:}\,t \approx 10^2{:}\,1$, could be achieved. Scanning electron micrographs (SEM) of Si nanoresonator devices from top and side-views are depicted in the images shown in Fig. 2a-b. To achieve these extreme aspect ratios, the most critical steps in the fabrication process (Fig. 1b) are (a) the nanobeam patterning with electron-beam lithography (EBL), and (b) the deep-reactive-ion-etching (DRIE) of Si. We used a state-of-the-art EBL equipment (Elionix, ELS-F130HM) for optimizing the dose and development time carefully to achieve the high aspect ratio metal patterns with global alignment marks patterned by the photolithography process done prior to this step. Several process parameters in the DRIE process, such as, bias-voltage and process times were optimized especially for the anisotropic etching of Si.

4.2 Resonance characteristics and Q-factor

After successful fabrication, the fabricated devices are mounted inside vacuum chambers and actuated by the method described in section 3. Resonance characteristics of the developed Si nanoresonators are characterized by measuring the vibration amplitude of the nanoresonators at different actuation frequencies around the vibration of fundamental, in-plane, bending mode vibration. This is achieved by conducting a frequency sweep of the ac actuation voltage. A typical actuation frequency versus amplitude (squared) plot is shown in Fig. 2c. A Lorentzian fit on the acquired data is used to identify the resonance frequency (f_0) as the center position of the peak and the quality factor (Q) is estimated from the full-width-at-half-maxima (FWHF) as $Q = f_0/\mathrm{FWHM}$.

We observed that the resonance frequency of our ultra-thin Si nanoresonators significantly deviates from the prediction (f_{EB}) of Euler-Bernoulli theory for stress-free elastic beams, indicating a dominant influence of an axial tensile stress (10 – 100 MPa) in determining the resonance frequency (f_0). (f/f_{EB}) ranges from 2 – 10 depending on the thickness of the nanoresonator.

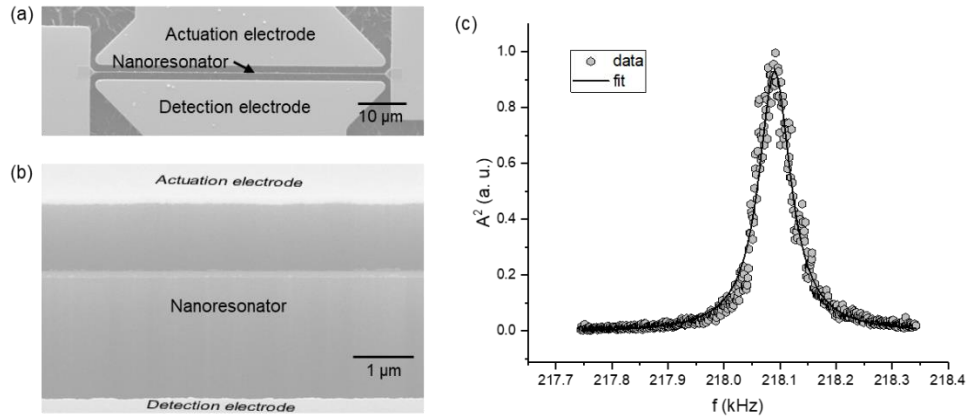


Fig. 2: Scanning electron micrographs (SEM) of Si nanoresonator devices (before release) taken from (a) top-view, and (b) side-view; (c) resonance peak acquired from a Si nanoresonator device fabricated for this study. (Note: Figures a, b, c are associated with different nanoresonators).

As t/L^2 of the nanoresonators decreases f/f_{EB} of the nanoresonators are observed to increase, indicating a gradual transition from a 'beam-like' to a 'string-like' dynamic behavior (Nano Lett. **23**, 11517–11525 (2023)). The room-temperature quality factor (Q) of the Si nanoresonators are found to be typically a few thousands. $Q \sim 10^3$ is almost an order of magnitude lower than our Si microresonators of similar design and structure. This deterioration of the Q at nanoscale happens for resonators below $t = 1$ μm. We performed a comprehensive theoretical and numerical analysis to understand the dominant mechanism for mechanical energy loss in our Si nanoresonators. By conducting experiments in various pressure, temperature conditions and on nanoresonators of different dimensions, and fitting various theoretical models and numerical analyses, we could establish surface loss as the likely dominant loss mechanism in the ultra-thin Si nanoresonators (at high vacuum). We observed a significant increase in Q of a Si nanoresonator at low temperatures (T) and an increase in resonance frequency (Fig. 3).

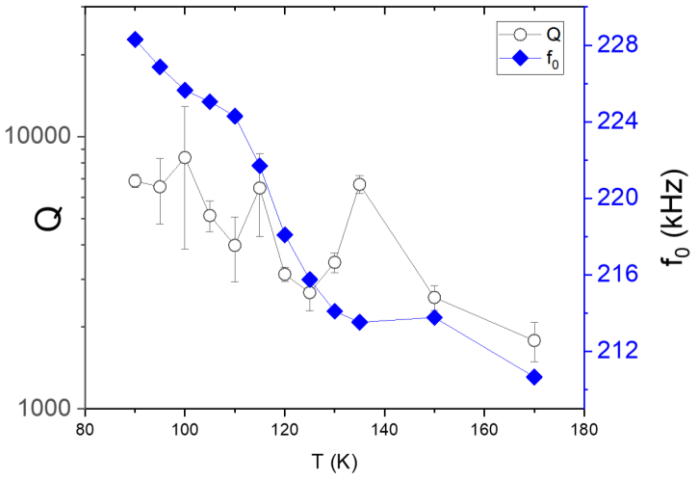


*Fig. 3: Variation of Q-factor and resonance frequency (f_0) of a Si nanoresonator measured as a function of device temperature (T). Further details and discussion are available at Nano Lett. **23**, 11517–11525 (2023).*

4.3 Electromechanical characteristics

A significant disadvantage of top-down fabricated Si nanoresonators compared to atomically thin nanoresonators is the lack of electrostatic tunability. In nanoresonators made from atomically thin materials, such as, graphene, MoS_2 etc. resonance frequency can be tuned (often ~ 100% of initial frequency) by simply tuning the dc gate voltage (V_{dc}) at room-temperature. This can bring an enormous amount of flexibility in various applications, where the resonator's frequency can be tuned on the spot to meet various requirements. Because of their ultra-thin structures (leading to small elastic stiffness), our Si nanoresonators can significantly mechanically deform (the center point comes closer to the actuation electrode) at reasonable gate-voltages (V_{dc}). Exploiting this feature, we have shown that ultra-wide room-temperature electrostatic resonance frequency tunability is also achievable in top-down fabricated Si nanoresonators. In Fig. 4a and 4b, we show the resonance frequency behavior of nanoresonators of 200 μm lengths and 300 nm, 40 nm widths, respectively, acquired at various V_{dc}. In Fig. 4a, a resonance frequency tuning range of about ~ 9% of initial frequency is observed, whereas in Fig. 4b, ~ 70% tuning range is seen. These values are quite atypical (large) compared to what is usually reported for top-down fabricated resonators. We have proposed a theoretical model to explain these trends based on electrostatic softening effect (responsible for downward tuning) and the stretching of the beam (responsible for upward tuning). Besides resonance frequency, we report ultra-wide tunability in the nonlinear behavior of our Si nanoresonator devices. We can significantly tune the cubic nonlinearity by gate-voltage.

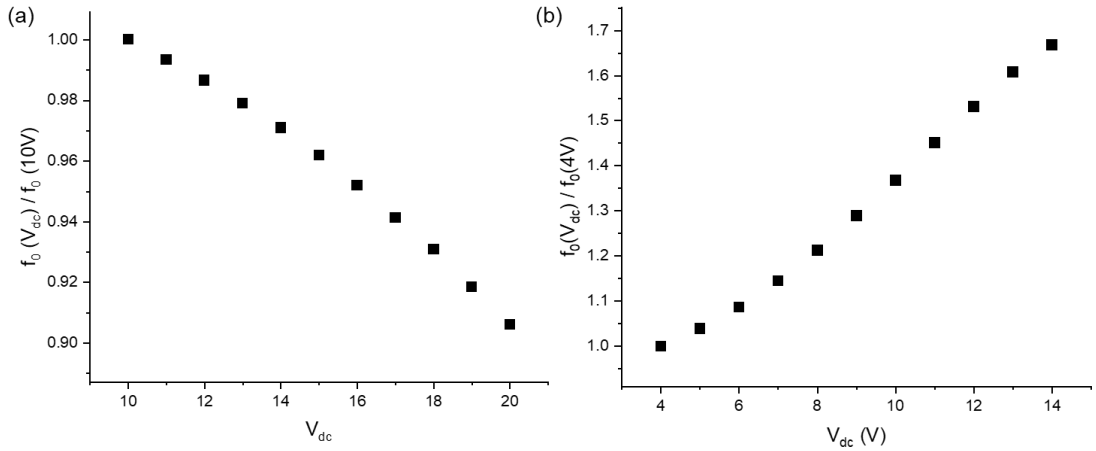
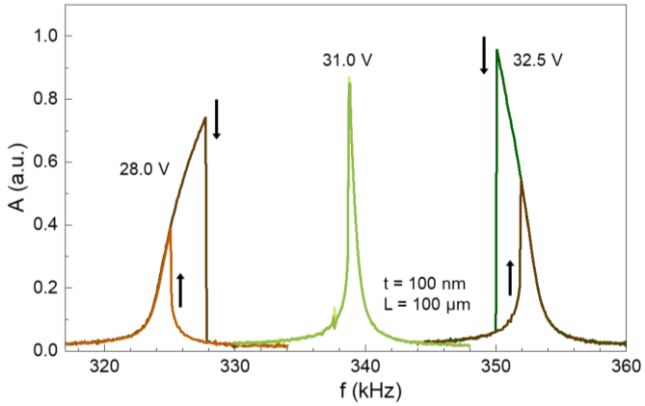


Fig. 4: Ultrawide tuning of resonance frequency of Si nanoresonator of L = 200 µm, and (a) t = 300 nm, (b) t = 40 nm showing ~ 9% (downward) and ~ 70% (upward) tuning of initial frequency. Further details and discussions are provided in Nano Lett. ***23****, 11517–11525 (2023).*



In the following figure (Fig. 5), we show in a nanoresonator of ~ 100 nm width, how the cubic nonlinearity coefficient is positive at V_{dc}= 28.0 V, then it is nearly cancelled (and linearity is restored) at V_{dc}= 31.0 V, then its sign is flipped, and a negative cubic stiffness is achieved. The ultrawide tunability of resonance frequency and nonlinearity can be very beneficial for mass sensing applications involving nanoresonators, where the sensitivity and resolution can be enhanced or tuned simply by tuning the V_{dc} as we discussed in the article published in the Japanese Journal of Applied Physics 63, 03SP74 (2024).

Fig. 5: Ultra-wide electrostatic tunability of the cubic nonlinearity coefficient in a Si nanoresonator device with L = 100 µm, t = 100 nm. Further details and discussion are available at Nano Lett. ***23****, 11517–11525 (2023).*

4.4 Gas-sensing study

We developed an experimental setup for performing gas-sensing experiments using our Si nanoresonators (Fig. 1a). Here, we chose to perform gas-sensing experiments using CO_2 with N_2 as a background. One motivation for choosing CO_2 is that it might act as a maker for detecting H. Pylori infection by analyzing the contents of human breath. Initially, the resonator is put inside the chamber and an initial resonance peak is achieved, as shown in Fig. 6. Then, CO_2 gas from a cylinder is introduced in the chamber (in steps of 2 seconds long exposure). Introduction of CO_2 gas is expected to do two things, (a) it reduces the Q-factor (by increasing air-damping) and (b) it increases the mass of the resonator, thus, lowers the resonance frequency. Both these effects are observed in Fig. 6 as CO_2 exposure is gradually increased. The shift for 2s exposure is roughly equivalent to a mass-change of ~ 10^{-15} kg, indicating that our Si nanoresonators have the potential to act as ultrasensitive gas sensors. However, we could not establish an effective method to functionalize the surface of the nanoresonator to make it selectively bind to CO_2 (over other gases in the environment). The primary challenge we faced is that the majority of the surface area of the nanoresonator is located at the sidewalls of microscopic trenches. Thus, the alignment of the surface is such that the deposition of thin-films becomes quite challenging.

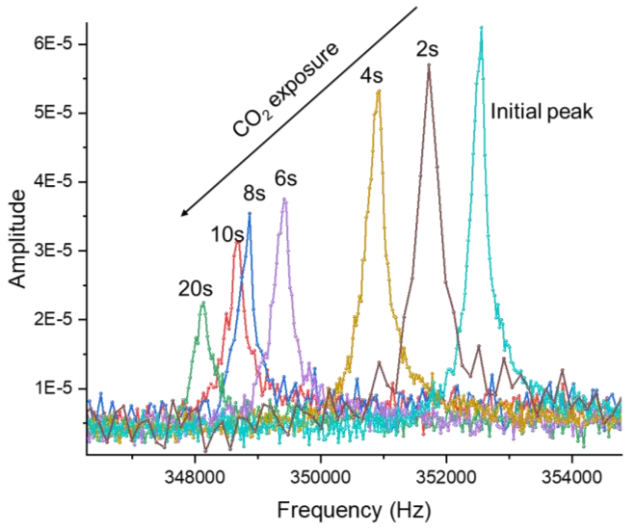


Fig. 6: Experimental demonstration of resonance frequency shift of a Si nanoresonator as a result of CO_2 exposure.

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　1件／うち国際共著　0件／うちオープンアクセス　1件）

１．著者名 Yu Wei、Ohara Yuma、Meffan Claude、Hirotani Jun、Banerjee Amit、Tsuchiya Toshiyuki	４．巻 23
２．論文標題 Achieving Ultrawide Tunability in Monolithically Fabricated Si Nanoresonator Devices	５．発行年 2023年
３．雑誌名 Nano Letters	６．最初と最後の頁 11517～11525
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.nanolett.3c03164	査読の有無 有
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１．著者名 Yu Wei、Banerjee Amit、Hirotani Jun、Tsuchiya Toshiyuki	４．巻 63
２．論文標題 Enhancing responsivity and detection limit in tunable nano-electromechanical system resonator mass sensors	５．発行年 2024年
３．雑誌名 Japanese Journal of Applied Physics	６．最初と最後の頁 03SP74～03SP74
掲載論文のDOI（デジタルオブジェクト識別子） 10.35848/1347-4065/ad2979	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

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３．学会等名 36th International Microprocesses and Nanotechnology Conference (MNC 2023), Sapporo, Japan, (Nov. 14-17, 2023), 17B-2-1（国際学会）
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〔図書〕　計0件

〔産業財産権〕

〔その他〕
Ultrathin Si resonator for gas sensing
https://www.nms.me.kyoto-u.ac.jp/ultrathin-si-resonator/
Q-factor of Si nanoresonator
https://www.nms.me.kyoto-u.ac.jp/en/qfactor-si-nanoresonator/

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関