様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科研費
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研究課題名（和文）Elucidating the effect of boundary curvature on the wrinkling of thin suspended films by theory and experiment

研究課題名（英文）Elucidating the effect of boundary curvature on the wrinkling of thin suspended films by theory and experiment

研究代表者

ＪＡＮＳＳＥＮＳ　Ｓｔｏｆｆｅｌ（Janssens, Stoffel）

沖縄科学技術大学院大学・力学と材料科学ユニット・グループリーダー

研究者番号：００８１７６２９

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研究成果の概要（和文）：本プロジェクトは、極薄素材の端に生じる「しわ」の湾曲率の影響を、理論と実験により解明することを目指したが、研究過程にて、フェムト秒レーザーを用いて光学的にアクセス可能な任意長のナノチャネルを作成する技術を偶然発見した。このナノチャネルは、ナノ結晶ダイヤモンドフィルムとガラス基板の間に形成され、断面の幅と高さの比が約100のスリットと類似しており、高さは100nm以下で精密調整が可能である。我々は、このチャネル作成のレーザー加工のメカニズムを解明し、本技術を用いたフィルムのパターニングも実証し、さらなる応用可能性を検証するため、コストや時間を削減できるナノ流体デバイスの製造技術開発を行った。

研究成果の学術的意義や社会的意義
The project is of fundamental scientific significance for various applications, such as designing nanofluidic devices for biomolecule detection.

研究成果の概要（英文）：This project was undertaken for the purpose of wrinkle research. During the course of this research, we accidentally discovered a technique for fabricating optically accessible nanochannels of arbitrary length using a femtosecond laser. These nanochannels are formed between a thin film of nanocrystalline diamond and a glass substrate, their cross-section resembles a slit with a width-to-height ratio of approximately 100, and their height can be precisely tuned at less than 100 nm. We were able to elucidate the laser processing mechanism that creates the channels, and we were able to demonstrate film patterning using the same technique. To validate the applicability of this research, we have developed nanofluidic devices that do not require the use of complex, costly, and time-consuming fabrication techniques.

研究分野：Nanocrystalline diamond

キーワード：wrinkling　nanocrystalline diamond　femtosecond laser　nanochannel　nanofluidics　delamination

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

With this project, we aimed to elucidate the effect of boundary curvature on the wrinkling of thin suspended films by theory and experiment. Much of the project involved developing a method for fabricating such structures using next-generation sustainable technologies. We successfully established such a method; however, while doing so, we serendipitously discovered a simple method for fabricating nanochannels. Most of the remaining time of the project was then invested in disseminating the nanochannel fabrication method. The method for making wrinkled structures was also used to fabricate a nanofluidic device comprised of open microchannels and closed nanochannels.
Nanofluidic channels, which have one dimension below the 100 nm cornerstone, are typically fabricated by combining techniques such as electron beam lithography, focused ion beam milling, reactive ion etching, thin-film evaporation, photolithography, and thermal bonding [1]. Such traditional techniques can yield durable devices but are complicated, expensive, and time-consuming, hindering progress in the field [2]. Still, recent progress in nanofluidics, which affords fundamental discoveries, energy-harvesting technologies, drug delivery, and biological analysis [3,4], provides ample reasons for finding novel approaches to fabricating nanochannels.
The direct femtosecond laser writing of nanochannels has the potential to substantially reduce the issues related to traditional fabrication techniques. Still, it has been a persistent challenge due to the small length scales involved. However, inspiring progress towards meeting this challenge has been made. Liao and coworkers [5] demonstrated the formation of sub−50 nm nanochannels in porous glass. However, the glass had to be thermally treated at approximately 1393 K to make the channels useful for applications, and the method did not enjoy subsequent development. Temnov and coworkers [6] demonstrated the formation of nanocavities in thin nickel films. Films that contain these cavities may provide ample opportunities for magnetism-related research. However, due to their lack of optical accessibility, it is difficult to interrogate their content. Lu and coworkers [7] demonstrated the formation of nanochannels in fused silica substrates through material ejection. Because of this mechanism, a channel forms a blind hole with cross-sections that differ in diameter but can be no more than 10 µm long, which strongly restricts device fabrication.

２．研究の目的

The aim of this project morphed into fabricating nanochannels by direct femtosecond laser writing due to a fortunate stroke of serendipity. The fabrication process is studied deeply to understand the physical/chemical processes during laser writing. To verify that the channels conduct liquids, we fabricated a nanofluidic device and observed the filling of the channels through capillary action. The project is of fundamental scientific significance for various applications, such as designing nanofluidic devices for biomolecule detection.

３．研究の方法

The material platform for direct femtosecond laser writing of optically accessible nanochannels with arbitrary lengths and slit-like cross-sections is a nanocrystalline diamond (NCD) film grown on a glass substrate. Nanochannels are formed between an NCD film and a glass substrate. The nanochannels created this way have cross-sections with a maximum height below 100 nm and widths on the order of micrometers. The shape of the nanochannels is investigated with atomic force microscopy (AFM). Laser-induced morphology changes are investigated using Raman spectroscopy and scanning electron microscopy (SEM). The presence of nanochannels and liquids in the channels is investigated using reflectance data obtained by confocal laser microscopy that is compared with reflectance simulations based on the AFM data. The schematic for fabricating a nanofluidic device is provided in Figure 1.

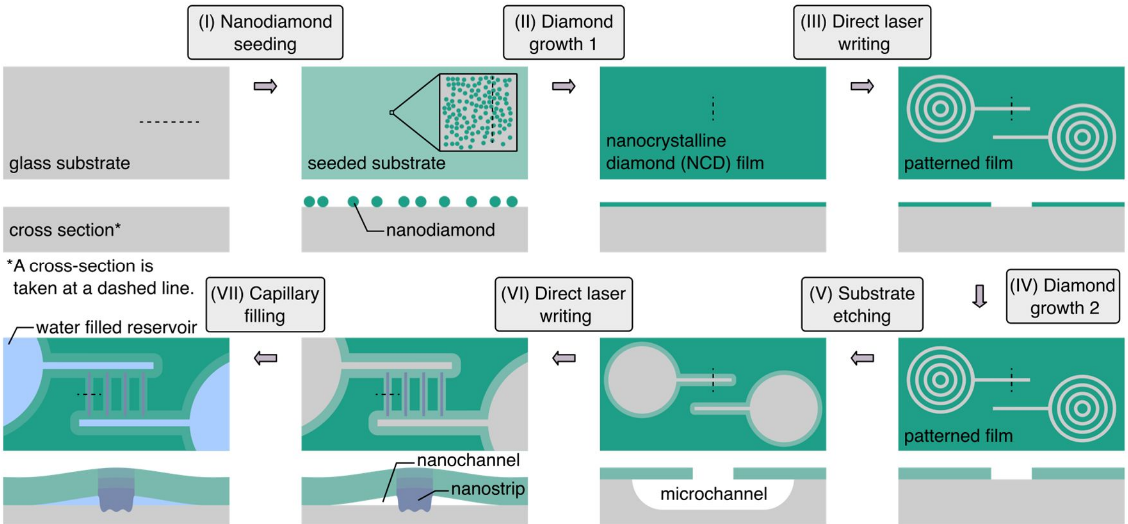

Figure 1 In step I, we seed a glass substrate with nanodiamonds. In step II, we deposit diamond on these grains with chemical vapor deposition until a closed nanocrystalline diamond (NCD) film is formed. In step III, we pattern the film through laser writing. The film is kept relatively thin, so patterning can be done at relatively low laser power to minimize substrate damage. In step IV, we increase the thickness of the films. In step V, we etch the substrate with a hydrofluoric acid-based mixture, transforming the concentric patterns into reservoirs and the straight-line patterns into open microchannels. In step VI, we connect the microchannels through the direct laser writing of nanochannels — more information on the shape of the channels is provided in the discussion below. In step VII, we deposit water in the reservoirs, and due to capillary action, the channels fill with water.

4．研究成果

We established the direct femtosecond laser writing of optically accessible nanochannels with arbitrary lengths. They exist between NCD films and glass substrates, and their cross-sections resemble slits with width-to-height ratios on the order 100. The heights of such channels can be tuned precisely below the 100 nm cornerstone. We focused on understanding the mechanisms involved and showcased film patterning using the same technique. To demonstrate that our findings apply to the fabrication of devices, we designed and made a nanofluidic device while circumventing traditional fabrication techniques, which are often complex, expensive, and time-consuming.

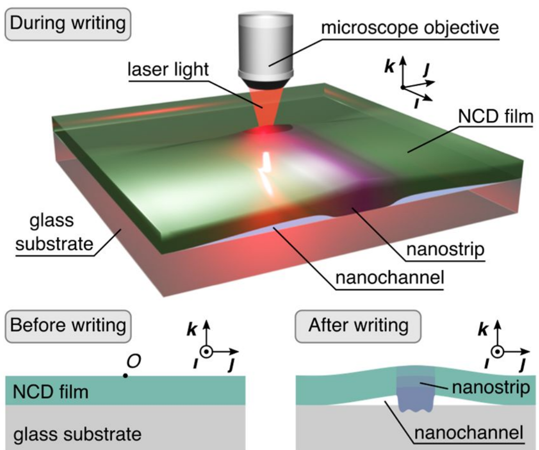

Figure 2 Schematic representation of direct femtosecond laser writing of nanochannels between an NCD film and a glass substrate.

As schematically represented in Figure 2, we found that laser writing can convert a portion of the sample into a nanostrip and that this phenomenon is induced by the expansion of sample material. The nanostrip is flanked by two nanochannels, formed through film delamination, and contains non-diamond carbon that plays a crucial role in supporting the delaminated film portions. This non-diamond carbon is formed when diamond changes into a different carbon allotrope. The nanostrip also consists of NCD and glass particles, which might be mixed with carbon. Our experiments demonstrated that nanostrip formation is initiated in a portion of the NCD film near the film—substrate interface. This might be traced to the presence of low-quality NCD in that vicinity, which is bound to absorb more light than high-quality NCD. If so, an NCD film on a glass substrate can be conceived as a three-layer system in which a relatively strong light-absorbing layer (low-quality NCD) is located between a relatively weak light-absorbing layer (high-quality NCD) and another layer (glass). Such samples may be fabricated with various materials and then used for the direct laser writing of embedded nanostructures with desired properties.

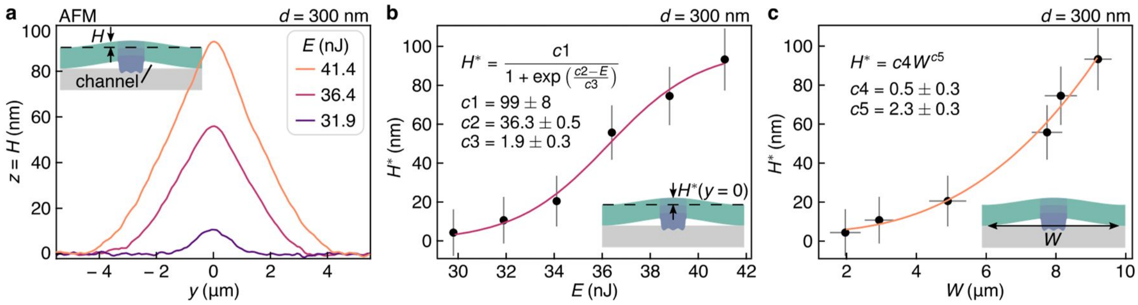

Figure 3 (a) Sample—air interface height H of structures obtained by laser writing plotted versus y. See Figure 2 for the orientation of the coordinate system. H is calculated by averaging atomic force microscopy (AFM) data. From these results, the cross-sectional dimensions of the nanochannels can be estimated. (b) Maximum height $H = H^*$ of the structure formed through laser writing, plotted versus laser pulse energy E. (c) H^* plotted versus the width W of the laser-written structures examined in (b).

Figure 3 shows that the height H^* of the nanostrip can be represented as a sigmoidal function of laser pulse energy E. We also found that H^* increases as the width W of the lasered structures increases, following an approximately quadratic power law. As a result, H^*/W grows as E increases. We also found that confocal laser scanning microscopy (CLSM) holds significant potential as a technique for sensing substances within optically accessible nanochannels when combined with specular reflectance simulations.

We demonstrated that relatively smooth patterns can be formed in samples through laser writing. This can be done if the NCD film is sufficiently thin (approximately 60 nm). Increasing film thickness requires more laser pulse energy, which leads to increased substrate damage and film delamination. We found that the probability of film fracture increases with laser pulse energy. Still, comparatively thick patterned films can be obtained while maintaining minimum substrate damage if diamond deposition is continued after patterning thin films.

Based on our findings regarding nanochannel writing and film patterning, we designed and fabricated a nanofluidic device with open microchannels that connect nanochannels and reservoirs. By filling the reservoirs with water, the microchannels were found to direct water to the nanochannels through capillary action, as confirmed with CLSM.

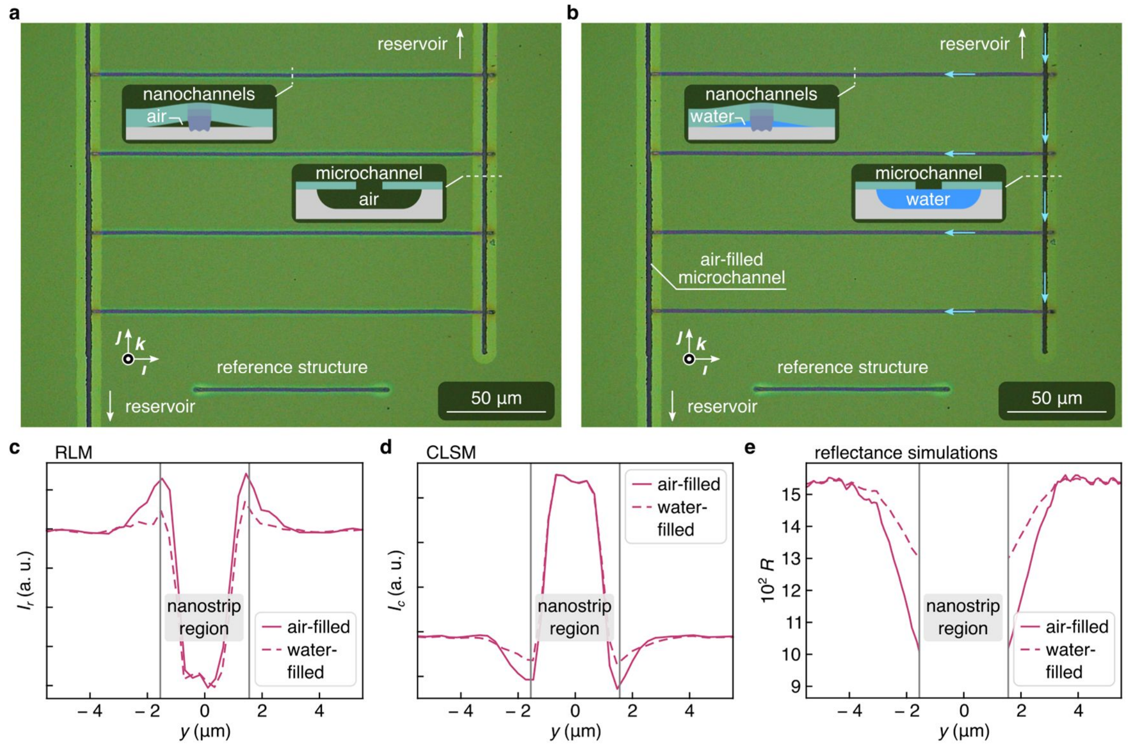

Figure 4 (a) Reflected light microscopy (RLM) image of an air-filled nanofluidic device. (b) RLM image with water-filled nanochannels. (c) RLM intensity I_r plotted versus y. (d) Confocal laser microscopy (CLSM) intensity I_c plotted versus y. (e) Specular reflectance R, obtained through simulations plotted versus y. The simulations support the presence of water in the nanochannels.

We showed that femtosecond laser writing provides an effective, high-precision means to create optically accessible nanochannels with arbitrary lengths and cross-sections with dimensions that differ by two orders of magnitude. Such channels find applications in various fields, including optofluidics, biosensing, and nanofluidics, where controlling and manipulating fluids, particles, or light at the nanoscale is essential. Our work was published in *Carbon* [8], and a patent was filed [9].

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[4] https://doi.org/10.1515/nanoph-2020-0310
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[9] PCT/JP2024/016586

５．主な発表論文等

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

1．著者名	4．巻
Janssens Stoffel D., Vazquez-Cortes David, Sutisna Burhannudin, Fried Eliot	215
2．論文標題 Direct femtosecond laser writing of nanochannels by carbon allotrope transformation	5．発行年 2023年
3．雑誌名 Carbon	6．最初と最後の頁 118455～118455
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.carbon.2023.118455	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

〔学会発表〕　計2件（うち招待講演　1件／うち国際学会　1件）

1．発表者名
Janssens Stoffel D.
2．発表標題 Direct laser writing of nanochannels between ultra-thin nanocrystalline diamond films and glass substrates
3．学会等名 2023 Materials Research Society (MRS) Fall Meeting & Exhibit（招待講演）（国際学会）
4．発表年 2023年

1．発表者名
Janssens Stoffel D.
2．発表標題 Direct femtosecond laser writing of nanochannels between nanocrystalline diamond films and glass substrates
3．学会等名 33rd International Conference on Diamond and Carbon Materials
4．発表年 2023年

〔図書〕　計0件

〔出願〕　計1件

産業財産権の名称	発明者	権利者
CHANNEL ELEMENT, PACKAGE, DRUG DELIVERY DEVICE, BIOMOLECULE TESTING APPARATUS, AND CHANNEL FORMING METHOD	JANSSENS Stoffel	同左
産業財産権の種類、番号 特許、PCT/JP2024/016586	出願年 2023年	国内・外国の別 国内

〔取得〕　計0件

〔その他〕

－

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
研究分担者	フリード　エリオット (Fried Eliot) (70735761)	沖縄科学技術大学院大学・力学と材料科学ユニット・教授 (38005)	

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