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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）実験・情報科学を統合した有機薄膜蒸着システム

研究課題名（英文）Creation of an organic thin film deposition system by integration of information science

研究代表者
Ｐａｃｋｗｏｏｄ　Ｄａｎｉｅｌ（Packwood, Daniel）

京都大学・高等研究院・講師

研究者番号：４０６４０８８４

交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：金属基板上の有機薄膜は有機エレクトニクス（OLEDなど)のための電荷輸送層として広く使用されている。このプロジェクトでは、高い結晶性を示す小分子薄膜につながる蒸着条件（蒸着時間、基板の温度など）を導く機械学習アルゴリズムを目指していた。・アルゴリズムのためのトレーニングデータを収集することができた。このデータが幅広い薄膜の状態（準単一層から～数層膜まで）にわたることを走査トンネル顕微鏡で確認した。しかし、アルゴリズムをうまく実行するにはさらなるのトレーニングデータが必要と分かった・また、有機薄膜に対する低速電子線回折パターンによって有機薄膜の構造を解明するための計算手法に成功した。

研究成果の学術的意義や社会的意義
・By minimizing trial-and-error, the algorithm will reduce the time required to deposit high-quality small molecule thin films, and might accelerate the development of organic electronics based upon small-molecule films.

・Organic thin film structure might be elucidated with our computational method.

研究成果の概要（英文）：Organic thin films on metallic substrates are widely used as charge transport layers in OLEDs (organic light emitting diodes) and other organic electronics.

In this project, we aimed to create a machine learning algorithm which can find the optimal deposition conditions for creating highly crystalline, small-molecule organic thin films. We succeeded to collect training data for this algorithm, and confirmed that it spans a wide range of thin film states (sub-monolayer to multilayer) using scanning tunneling microscopy. However, more training data is needed to run the optimization algorithm properly. In addition, we created a new computational method which can, in principle, determine the atomic structure of an organic thin film from low energy electron diffraction (LEED) data.

研究分野：計算材料科学

キーワード：有機薄膜　低速電子線回折　走査トンネル顕微鏡　低速電子線回折シミュレーション　ベイズ最適化　教師なし機械学習　薄膜構造の解明

１．研究開始当初の背景

Organic thin films on metallic substrates are widely used as charge transport layers in OLEDs (organic light emitting diodes) and other organic electronics. In order for such devices to perform efficiently, it is desirable for the thin film to have a minimal number of traps and defects, as these tend to localize charge carriers and impede charge transport.

At present, the organic thin films in commercial organic electronics are mainly prepared by spin-casting or coating polymer molecules. Polymer thin films can be prepared relatively easily and without cracks or macroscopic defects, however their charge carrier mobilities are usually too small for many applications.

Organic thin films can also be prepared by deposition of small organic molecules. Compared to polymer thin films, small molecule thin films tend to display much higher charge carrier mobilities. However, these high charge carrier mobilties usually require highly crystalline thin films. Unfortunately, highly crystalline small molecule thin films are very difficult to prepare, and considerable time is required to find the optimal parameters (deposition time, substrate temperature, and so on) leading to high crystallinity.

２．研究の目的

(Goal 1) *Create an algorithm which can quickly find the optimal parameters for depositing highly crystalline, small-molecule organic thin films under ultra-high vacuum conditions.*

By minimizing trial-and-error, this algorithm is expected to dramatically reduce the amount of time required to deposit high-quality small molecule thin films. If such an algorithm was taken up in industry, then it might accelerate the development of high-performance organic electronics based upon small-molecule thin films.

(Goal 2) *Create a computational method which can determine the atomic-level structure of small-molecule organic thin films from experimental electron diffraction data.*

The atomic-level structure of an organic thin film must be known in order to clarify charge transport mechanisms. Low-energy electron diffraction (LEED) provides the most precise information on thin film atomic structure, however for the case of organic materials (as opposed to metals) there are no reliable methods for transforming the LEED pattern from reciprocal space to real space.

The combination of Goal 1 and Goal 2 therefore allows us to create highly crystalline small molecule organic thin films with a known atomic structure.

３．研究の方法

(Goal 1)

In order to create the algorithm, a machine learning approach based upon Bayesian optimization was used. For a given organic molecule and substrate, a set of training data was collected. This training data consisted of thin film deposition time, substrate annealing temperature, substrate annealing time, and LEED patterns collected at various electron energies. Deposition was performed *via* molecular beam epitaxy from a Knudsen cell. A scanning tunneling microscope (STM) was acquired half-way through this project, allowing us to incorporate STM images into the training data as well. All data was collected under ultra-high vacuum conditions.

(Goal 2)

Our computational method consisted of a real-space quantum dynamics simulation of an electron pulse colliding with a surface. By using a surface potential calculated from accurate first-principles calculations (as opposed to simple localized potentials from other methods), our method is reliable for the case of organic molecule thin films. Real-space quantum dynamics simulations were performed by direct integration of the time-dependent Schrodinger equation using an in-house code. Surface potentials were calculated using density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP).

４．研究成果

(Goal 1)

During FY2019, we collected training data for the case of a copper(111) (Cu(111)) substrate and (9,9')-bianthracene (bianthracene) deposited by molecular beam epitaxy. Bianthracene is a representative material for organic electronics, and closely related compounds are used in OLEDs (e.g., Se *et al. Dyes and Pigments* **148**, 2008, 329) and for graphene nanoribbon fabrication (Cai *et al. Nature* **466**, 2010, 470). To collect this training data, bianthracene was deposited using various deposition times (10 seconds to 10 minutes) at various substrate temperatures.

LEED patterns and STM images showed that our training data covered a range of molecular coverages and thin film thicknesses. Clear STM images showing bianthracene molecules aligned at Cu(111) step edges could be obtained, indicating that our training data contains cases from the sub-monolayer regime. Somewhat clear STM images could also be obtained for the cases of multi-layer thin films. These multilayer thin films appeared to have a laminar structure (with structural order persisting over ~100 nm distance). While this intrinsic structural order improved with high-temperature annealing, the alignment was not perfect and no clear LEED pattern could be measured from them. Examples of STM images and LEED patterns from this training data are available upon reasonable request (at time I writing, we cannot access this data due to restrictions arising from the COVID-19 epidemic).

In addition to this training data, the basic Bayesian optimization algorithm for analyzing this data is available and will be used to predict the condition to obtain a highly crystalline monolayer bianthracene thin film. However, in our training data, we unexpected observe only two behaviors for the LEED pattern: either the background Cu(111) peaks are completely absent in the multi-layer regime, or are very intense in the submonolayer regime but change little with increasing coverage. Because mathematical optimization requires a response variable which varies smoothly with changes in deposition conditions, the LEED patterns in our training data cannot be used for optimization. While this finding has delayed the research plan, I am currently investigating whether STM images could be used in place of LEED patterns for the optimization. Moreover, I am trying to obtain deposit monolayer bianthracene thin films, from which clearer changes in LEED pattern should be observed. I aim to have

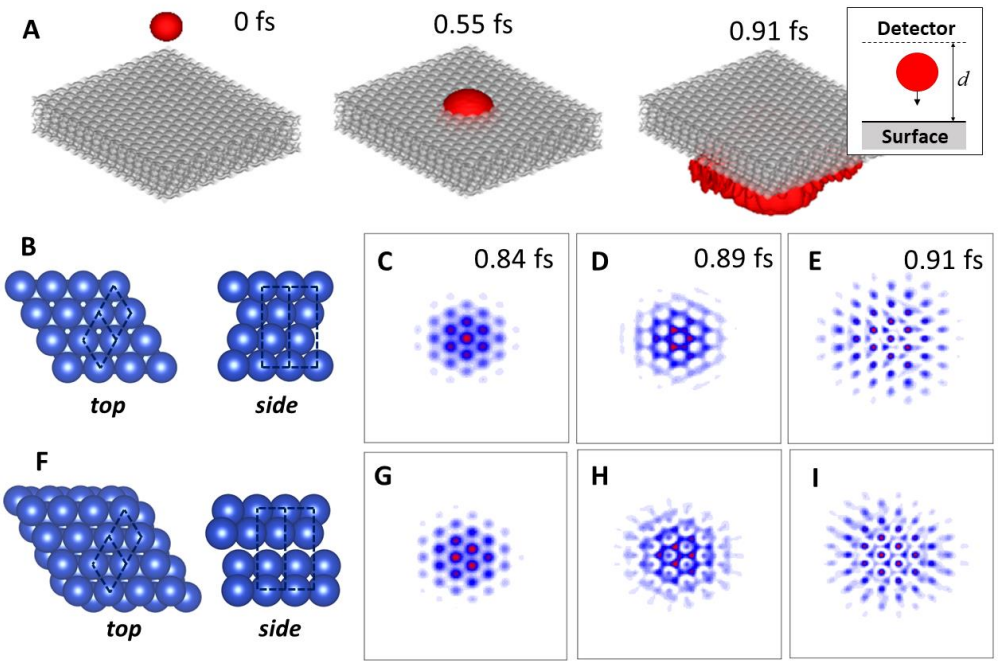

Figure 1. (A) Electron pulse (red) traveling towards a Cu(111) surface (grey). The time since the beginning of the simulation is indicated. The insert shows the position of the detector. (B) Structure of Cu(111). Blue spheres are Cu atoms. Dotted lines indicate unit cell shape. (C – D) Time-dependent electron diffraction pattern for the Cu(111) surface. Red, blue, and white indicate areas of high, low, and zero intensity, respectively. (F) Configuration of Cu atoms having the same symmetry as Cu(111) but different atom positions. (G – I) Time-dependent electron diffraction pattern for the structure in (F). Image taken from Packwood, *Sci. Rep.* **10,** 2020, 5868. See that paper for more details.

this complete before the summer of this year. .

(Goal 2)
Figure 1 (taken from Packwood, *Sci. Rep.* **10,** 2020, 5868) illustrates our electron diffraction simulations for the case of a bare Cu(111) surface. Figure 1A plots the square amplitude of the electron wave packet (red) and the surface potential (grey) at various time since the start of the simulation. Figure 1B shows the structure of pristine Cu(111), and Figure 1C – 1E show the time-evolution of the electron diffraction pattern as electrons scatter from the surface and pass through the detector. This sub-femtosecond time evolution cannot be observed in a real experiments, because experimentally the diffraction pattern is averaged over a long time scale (microseconds to seconds). Figure 1F shows a random configuration of Cu atoms with the same symmetry as Cu(111), and Figures 1G – 1I show the time-evolution of the corresponding electron pattern. It can be seen that the two copper structures (1B and 1F) give rise to distinct time-dependent diffraction patterns (1C – 1E, and 1G – 1I, resp), despite sharing the same symmetry.

In order to rigorously confirm that time-dependent diffraction (TD-LEED) patterns are indeed sensitive to the atomic configuration of the surface, we performed electron diffraction simulations for numerous random Cu configurations and also a chemisorbed thiol-alcohol layer on Au(111). For each system, all candidate configurations possessed the same symmetry, but differed in the locations of the atoms. By judicious application of hierarchical clustering analysis, we could confirm that TD-LEED patterns from both bare metals and organic thin film surfaces are indeed highly sensitive to atomic configuration.

The high sensitivity of the TD-LEED patterns to atomic configurations means that they can be used to determine organic thin film structure from experimental LEED patterns. Providing that a highly crystalline organic thin film is successfully fabricated from Goal 1 above, we could measure the LEED patterns at a variety of energies (this is called the LEED-I(V) method). These LEED patterns can then be transformed to the time-domain by applying the transformation reported by Yan *et al* (Yan *et al. Phys. Rev. B.* **84**, 2011, 224117). Then, by comparing these experimental time-domain images with the TD-LEED patterns simulated with our method, we will be able to find the atomic configuration which agrees with the experimental data most closely. Once we obtain a highly crystalline bianthracene thin film from Goal 1, we proceed in this direction

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 Daniel M. Packwood	４．巻 10
２．論文標題 Exploring the configuration spaces of surface materials using time-dependent diffraction patterns and unsupervised learning	５．発行年 2020年
３．雑誌名 Scientific Reports	６．最初と最後の頁 5868 - 5879
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41598-020-62782-6	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6件（うち招待講演　6件／うち国際学会　3件）

１．発表者名 Daniel Packwood
２．発表標題 Low-energy electron diffraction from organic monolayers
３．学会等名 SPIRITS International Symposium 2019 - Regulation of cell fate and disease treatment（招待講演）
４．発表年 2019年

１．発表者名 Daniel Packwood
２．発表標題 Machine learning for nanomaterials assembly on surfaces
３．学会等名 Interfacing Machine Learning and Experimental Methods for Surface Structures（招待講演）（国際学会）
４．発表年 2018年

１．発表者名 Daniel Packwood
２．発表標題 Structure prediction and control for functional surface materials
３．学会等名 Applied Math for Energy: Future Directions (I2CNER, Kyushu University)（招待講演）
４．発表年 2020年

１．発表者名
Daniel Packwood

２．発表標題
表面上の分子集合体のための機械学習

３．学会等名
近畿化学協会コンピューター化学部会　第107回例会（招待講演）

４．発表年
2020年

１．発表者名
Daniel Packwood

２．発表標題
Informatics for self-assembled materials

３．学会等名
First Max Planck-VISTEC Symposium on Materials Science (VISTEC, Thailand)（招待講演）（国際学会）

４．発表年
2019年

１．発表者名
Daniel Packwood

２．発表標題
Machine learning for surface-assisted self-assembly

３．学会等名
NANOMAT2019 (CNRS, France)（招待講演）（国際学会）

４．発表年
2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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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