

SOLID STATE CHEMISTRY

Annual Research Review

(1) "Nano-scale anodic oxidation on a Si(111) surface terminated by bilayer-GaSe"

We fabricated nano-scale oxide patterns on a bilayer-GaSe terminated Si(111) (BGS) surface using an atomic force microscope (AFM) in air. The Si(111) surface regularly terminated by bilayer-GaSe is very stable in air, although it can be oxidized through the electrochemical reaction when positive sample bias voltage is applied between the surface and a conductive cantilever tip of AFM. It has been revealed that higher sample bias voltage, slower tip velocity and/or higher ambient humidity produce wider and/or thicker oxide protrusions. Then, nano-scale oxide patterns as narrow as 50 nm have been successfully drawn on the terminated surface by adjusting these experimental conditions. These oxide lines can be etched away by dipping the sample into aqueous HF solution, and nano-scale grooves can be fabricated on the bilayer-GaSe terminated Si(111) surface.

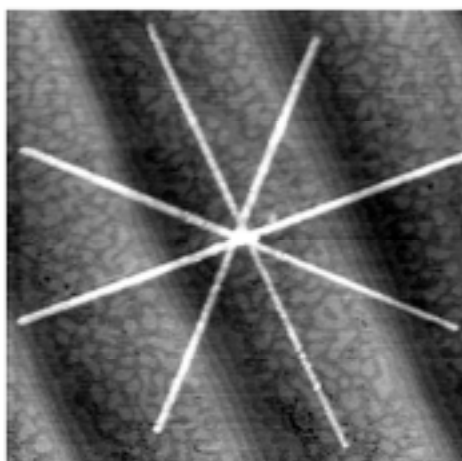


Fig. 1 AFM image (5 μm \times 5 μm) of typical oxide lines drawn on a BGS surface by the AFM anodic oxidation process in air. Sample bias voltage: +8 V, tip velocity: 250 nm/s.

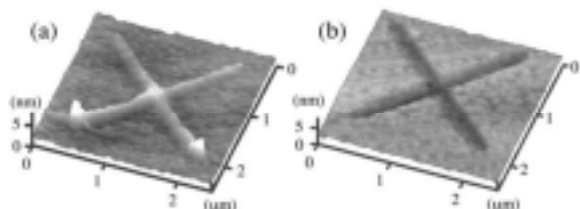


Fig. 2 AFM images of oxide lines fabricated on the BGS surface (a), and after the etching in 2% aqueous HF solution for 1 min (b).

A-9) *Surf. Sci.* **514** 27-31 (2002)

(2) "Electron spectroscopy of organic thin film device structures"

Electronic devices based on organic semiconductors are important for the application to mechanically flexible and printable electronic circuits. The intrinsic limit of the device performance is determined by the nature of charge carriers, which is not fully understood. In order to study the molecular nature of charge carrying species, we have attempted to apply electron spectroscopic techniques to working organic thin film devices. Figure 3 shows the C₆₀ thin film field effect transistor (FET) structure for the measurement. It was found that ultraviolet photoelectron spectra (UPS) can be measured when the gate bias voltage was not less than 20V as shown in Fig. 4, which makes n-type semiconductor C₆₀ conductive. Time-dependent irreversible change was observed by continuous UPS measurement and that kind of behavior has not been reported on C₆₀ films grown on conductive substrates. From the plasmon energy shift in electron energy loss spectroscopy, it was suggested that this change was due to photopolymerization of C₆₀ that was enhanced by fabricating a FET structure.

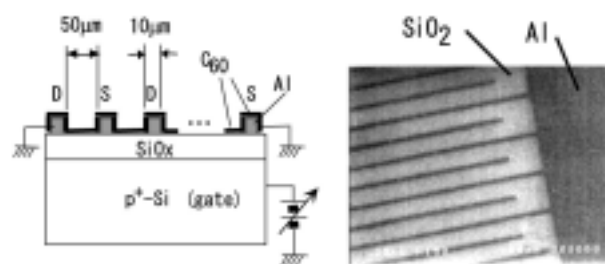
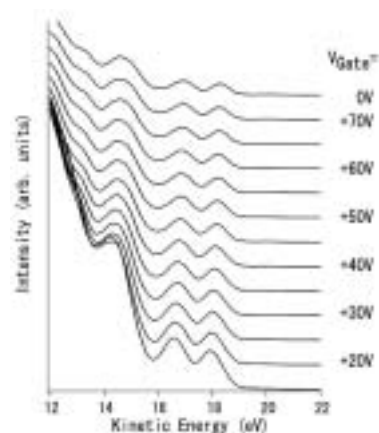


Fig. 3 C₆₀ thin film FET structure for the electron spectroscopy measurements

Fig. 4 Ultraviolet photoelectron spectra of C₆₀ thin film FET under gate bias voltages.



A-5) *Jpn. J. Appl. Phys.* **41** 2724-2726 (2002)

固体化学研究室

研究レビュー

(1) Bilayer-GaSe で終端した Si(111)表面上への陽極酸化ナノ構造形成

Bilayer-GaSe で規則的に終端した Si(111)表面 (BGS 表面) 上に, 原子間力顕微鏡 (AFM) を利用してナノスケールの酸化物パターンを形成することを試みた。この表面は大気中でも非常に安定であるが, AFM の導電性カンチレバーと試料表面間にバイアス電圧を加えて走査することにより, 表面を局所的に酸化することができる。試料に対し正の高い電圧を加えたり, 走査速度を遅くしたり, あるいは高湿度下で走査した場合には, 厚く, 幅の広い突起状の酸化物パターンを生成することができた。これらの条件を制御することで, 最小 50nm 幅のパターン描画も可能である。この酸化物突起状パターンだけをフッ酸水溶液を用いて選択的に除去し, 同サイズの溝状パターンを形成することにも成功している。

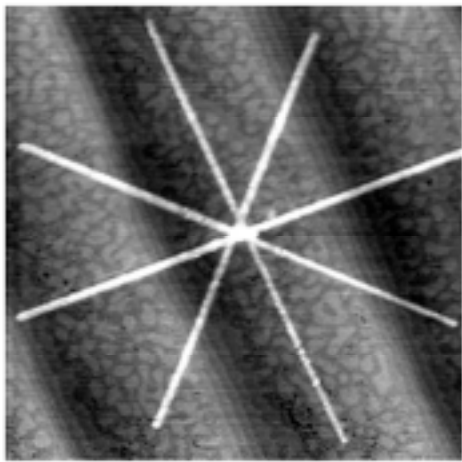


図1 BGS 表面上に AFM 陽極酸化法により形成した酸化物細線の AFM 像 (5 μm × 5 μm)。試料電圧: +8 V, 走査速度: 250 nm/s。

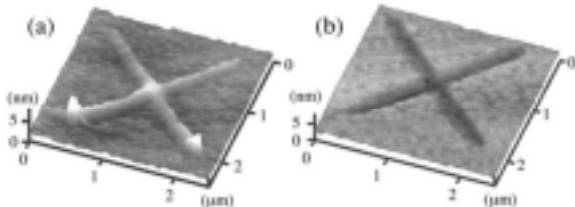


図2 BGS 表面上に形成した酸化物細線(a)と, 2% フッ酸水溶液で 1 分間エッチングしたあとの同じ場所(b)の AFM 像。

A-9) *Surf. Sci.* **514** 27-31 (2002)

(2) 有機半導体薄膜トランジスタの電子分光

有機半導体による電子デバイスは力学的にフレキシブルな電子回路をインクジェットプリントなど大量生産に適した手法で作成できるため, 近年活発に研究されている。様々な有機半導体中で電荷を運ぶものは何か, という問題は, 有機半導体素子の性能の上限を定めるものであり極めて重要であるがほとんどわかっていないのが現状である。この問題を探る系統的な実験手法を開発するため, 有機半導体薄膜トランジスタの電子分光を試みた。図3に示す構造の C₆₀ 薄膜電界効果トランジスタ (FET) 構造 (膜厚 2 nm) にゲート電圧をかけた状態で紫外光電子分光を測定したところ, 図4に示すようなスペクトルが得られ, 膜の電気伝導度が上昇するゲート電圧 20V 以上で電子分光の測定が可能であることが明らかになった。また, 測定中にスペクトルの経時変化が観察され, 電子エネルギー損失分光の結果から C₆₀ の光重合が起こっていることが示唆された。このような変化は導電性基板上に成長した C₆₀ では観察されないことから, FET 構造により光重合が促進されているものと考えられる。

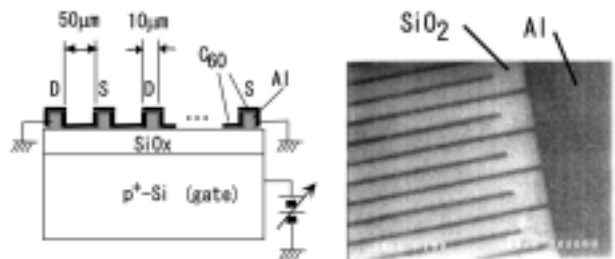
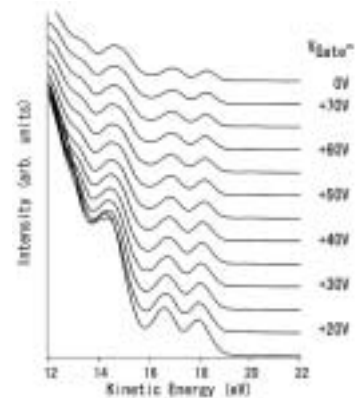


図3 測定に使用した C₆₀ 薄膜 FET 構造

図4 ゲート電圧をかけた C₆₀ 薄膜 FET 構造の紫外光電子スペクトル



A-5) *Jpn. J. Appl. Phys.* **41** 2724-2726 (2002)

A. Original papers

- 1) (M. Kiguchi), (K. Saiki) and A. Koma, "Heteroepitaxial growth of alkali halide solid solution on GaAs (001)", *J. Cryst. Growth* 237-239, 244-248 (2002).
- 2) (M. Katayama), (M. Kiguchi), (K. Saiki) and A. Koma, "Atomic and Electronic structure of LiF/LiBr(001) interface", *J. Cryst. Growth* 237-239, 269-273 (2002).
- 3) K. Ueno, S. Tokuchi, (K. Saiki) and A. Koma, "Epitaxial growth of a vacancy-ordered Ga₂Se₃ thin film on a vicinal Si(001) substrate", *J. Cryst. Growth* 237-239, 1610-1614 (2002).
- 4) (M. Kiguchi), (K. Saiki), A. Koma, "Dynamic and Static Disorder of Alkali Halide Solid Solutions studied by Temperature-dependent Extended X-ray-Absorption Fine Structure", *J. Phys. Soc. Jpn.* 71, 1076-1082 (2002).
- 5) T. Shimada and A. Koma, "Electron spectroscopy of C₆₀ thin film FET structures", *Jpn. J. Appl. Phys.* 41, 2724-2726 (2002)
- 6) K. Ueno, H. Shirota, T. Kawamura, T. Shimada, (K. Saiki) and A. Koma, "Highly-stable passivation of a Si(111) surface using bilayer-GaSe", *Appl. Surf. Sci.* 90, 485-490 (2002).
- 7) (M. Kiguchi), (T. Goto), (K. Saiki), (T. Sasaki), (Y. Iwasawa), A. Koma, "Atomic and electronic structure of MgO/Ag(001) heterointerface", *Surf. Sci.* 512, 97-106 (2002).
- 8) (H. Asaoka), (Y. Machida), (H. Yamamoto), (K. Hojou), K. Saiki, A. Koma, "Stress evolution during epitaxial growth of SrO films on hydrogen-terminated Si(111) surfaces", *Solid State Commun.* 124 (2002) 239-242.
- 9) K. Ueno, R. Okada, (K. Saiki) and A. Koma, "Nanoscale anodic oxidation on a Si(111) surface terminated by bilayer-GaSe", *Surf. Sci.* 514, 27-32 (2002).
- 10) T. Shimada and A. Koma, "Prospects of electron spectroscopy of working organic electronic device structures", *ICICE Trans. Electron.* E85-C, 1330-1332 (2002).
- 11) K. Iizumi, (K. Saiki), A. Koma, "Investigation of the interaction between a C₆₀ epitaxial film and a Si(111)-7x7 surface by electron energy loss spectroscopy", *Surf. Sci.* 518, 126-132 (2002).
- 12) (M. Kiguchi), (S. Entani), (K. Saiki), (H. Inoue), A. Koma, "Two types of epitaxial orientations for the growth of alkali halide on fcc metal substrates", *Phys.Rev.B* 66 (2002)155424.

D. Books

- 1) T. Shimada and A. Koma: "Electronic Structure of Interfaces between Organic Molecules and van der Waals Surfaces" in "Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and Optoelectronic Applications", edited by R. Salaneck et al., Marcel Dekker, New York, 2002, pp841-869.
- 2) T. Shimada and A. Koma: "Preparation of Single Crystalline van der Waals Surfaces" in "Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and

Optoelectronic Applications”, edited by R. Salaneck et al., Marcel Dekker, New York, 2002, pp811-815.

- 3) 島田敏宏、上野啓司：“機器分析実験”東京化学同人(2002) 梅澤・本水・渡会・寺前編、第9章6節「低速電子回折」 p.339-345.