層状化合物を用いた高移動度フレキシブル電界効果トランジスタの開発に関する研究

Development of high-mobility flexible field effect transistors using layered structure compounds

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1. 研究の概要

本研究では，「柔軟性」と「高機能性」を併せ持つ薄膜トランジスタ（TFT）を，無機層状構造半導体のような，構造に異方性をもつ低次元物質を用いて開発することを目標として研究を進めている。

近年，有機半導体薄膜を用いて電界効果トランジスタ（FET）を形成する試みが数多く行われている。その応用上の目的としては，シリコンでは実現が難しい新奇素子を，有機半導体を用いて形成する，ということがある。既に市販されているような薄型ディスプレイのために用いられる TFT は，アモルファスシリコンや多結晶シリコンなどを材料として開発が進められており，この目的のために有機半導体を用いる必要性はほとんどない。しかし，いわゆる「電子ペーパー」と呼ばれるような折り曲げ可能な柔軟な表示装置は，堅い共有結合の存在が必要不可欠なシリコン素子では実現が難しい。一方，π電子系ネットワークを持つ有機半導体，特に高分子ポリマーは柔軟性を持ち，印刷のような手法により薄膜素子を高速／大量／安価に形成できる可能性があるため，電子ペーパー用 TFT 材料として注目を集めている。しかし，現段階の有機薄膜 FET は，性能（移動度，オンオフ比など）が良い「低分子蒸着法」で作製されたものであっても，その最高レベルでやっとアモルファスシリコン TFT の性能に届くか，といった程度である。動画の高速再生が可能な表示装置の作製にはさらなる高機能化が必須である。

有機薄膜 FET の性能向上を阻害する要因として，有機チャネル層内のπ電子系ネットワークの連続性が不十分で，ソース／ドレイン電極間に多数の欠陥が含まれている，ということが挙げられる。このような欠陥を減らし，キャリア移動障壁を減らすことができれば，FET 移動度の飛躍的な向上が望める。そこで本研究では，層内キャリア移動度の高さと柔軟性を併せ持つような物質を，有機物質に限ることなくさまざまに探索し，FET チャネル層として用いることを考えている。具体的には，層状遷移金属ダイカルコゲナイド，III-VI 層状化合物半導体，といった層状構造を持つ化合物半導体，あるいはグラファイト微結晶をチャネル層に用い，折り曲げ可能な薄膜 FET を作製する，という実験を進めている。

2. これまでの研究成果

(1) ゲート絶縁体として利用可能な層状構造化合物の検討

フレキシブルな薄膜電界効果トランジスタ（FET）のゲート誘電体として一般に用いられるプラスチックフィルムは，表面構造に秩序性が無く，そのまま基板として高品質なチャネル層を成長することは困難である。本課題では，絶縁性が高く，しかも柔軟性を併せ持つ層状ケイ酸塩化合物の白雲母単結晶に着目し，これをゲート誘電体として利用することを試みた。白雲母の劈開面上に真空蒸着によってペンタセンおよび C_{60} 薄膜をエピタキシャル成長し，トップコンタクト型のソース／ドレイン電極を形成して FET を作製しその特性を評価したところ，両物質とも結晶性の良い薄膜が成長することが確認され，ペンタセンはp型，C_{60} はn型の FET として動作した。現在は動作特性の向上に取り組んでいる。

(2) アモルファス基板表面上へのテンプレート構造転写

陽極酸化法により形成した Ta_2O_5 皮膜や熱酸化 SiO_x といった平坦な基板表面に PMMA 高分子薄膜をスピンコートし，さらにステップバンチ Si(111)テンプレート基板を鋳型として用いるインプリンティング法を適用することによって，アモルファスな基板表面に秩序性の高い nm スケールの周期的段差構造を転写することに成功した。この手法を柔軟なフィルム状基板表面に適用し，さらに周期構造に沿わせた高品質・低欠陥なチャネル層を有機半導体や無機層状半導体を用いて形成することによって，高移動度な FET の実現が期待できる。

(3) 薄片剥離法による単層 MoS_2 形成

単結晶 MoS_2 のファンデルワールス層間にグリニャール試薬を用いて Li をインターカレートし，さらに純水と反応させ水素を発生することで層間を剥離し，単層 MoS_2 を形成することを試みている。これまでに Li

のインターカレート，水素発生，及び MoS_2 粉末の変質までは確認を行っており，現在単層薄片の分離と基板上への堆積について実験を進めている。

３．発表論文および学会発表

研究成果（１）関連

・学術論文

“Fabrication of an Organic Field-effect Transistor on a Mica Gate Dielectric”, Akira Matsumoto, Ryo Onoki, Keiji Ueno, Susumu Ikeda, and Koichiro Saiki, *Chem. Lett.* **35** (2006) 354-355.

（論文の内容）

Abstract

We fabricated pentacene-based organic field effect transistors (OFETs) using single-crystalline natural mica substrates as the gate dielectric. Substrate temperatures during the deposition of pentacene films were varied from room temperature (RT) to 90 ºC. Epitaxial growth of the pentacene film on the mica surface was observed even at RT. The FET working characteristics on the mica gate dielectric have been observed for the first time.

1. Introduction

Recently, OFET has been widely studied and its device performance has been considerably improved.[1] In many studies of OFET, thermally grown SiO_x on a conductive Si substrate has been used as the gate dielectric, but the use of SiO_x sometimes limits the performance of OFET. For instance, the dielectric constant of SiO_x is rather low ($\varepsilon \approx 4$), which requires high operation voltage. To overcome this difficulty, many groups have studied high dielectric constant materials instead of SiO_x.[2-5] Another disadvantage to use SiO_x is its crystallinity, because a single-crystalline organic film could not grow on the amorphous SiO_x. The initial organic layer on the gate substrate mainly rules the working characteristics of OFETs.[6,7] Thus, the improvement of the crystallinity at the organic-gate dielectric interface is expected to decrease defects or grain boundaries, resulting in enhancement of the OFET performance.

In the present work, we tried to fabricate OFETs on layered material substrates. When an organic film is grown on a cleaved surface of the single-crystalline layered material, the crystallinity of the grown film is improved and its defects are reduced. Indeed, successful epitaxial growth of organic films on layered material substrates such as MoS_2, mica, GeS, etc., have been reported.[8-12] Here, we focus on “muscovite mica” as the gate dielectric of OFETs. Mica is less expensive than SiO_x, and its cleaved surface has excellent flatness and crystallinity. Mica has been used as a capacitor or an insulator in electric circuits for a long time. To our knowledge, however, mica was not utilized as the gate dielectric in OFETs so far. Thus, we tried to fabricate OFETs on mica gate substrates by depositing epitaxial films of pentacene, which is the most popular organic semiconductor for OFETs. We investigated the growth mechanism of pentacene films grown at different substrate temperatures, and evaluated the field-effect mobility by measuring the conductivity for various gate voltages.

2. Experimental

A natural mica (muscovite) substrate was cleaved using an adhesive tape in atmosphere to approximately 1 μm thick, and used as the gate substrate without further surface treatment. The gate electrode of Au was thermally deposited onto the backside of the mica substrate. As-purchased pentacene (98%, Aldrich Chem. Co.) was evaporated from a Knudsen cell onto the mica surface for 2 h under the ultrahigh-vacuum condition (ca. 10^{-7} Pa). The deposition rate was maintained at 1.2 $nm \cdot min^{-1}$ and the substrate temperature was set at RT, 60 or 90 ºC. The nominal thickness of the pentacene film was measured by a crystal quartz thickness monitor. Finally, source and drain electrodes of Au were formed by thermal deposition through a metal shadow mask placed on the pentacene film. The channel length (L) and width (W) in the top-contact OFET were 0.1 and 1.0 mm, respectively. Working characteristics of OFETs were measured in a vacuum desiccator (ca. 1 Pa). The morphology and the crystallinity of pentacene films on mica surfaces were investigated by atomic force microscopy (AFM), X-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED).

3. Results and discussion

Figure 1 shows the AFM images of pentacene films grown on the mica surfaces for various substrate temperatures and deposition times. In the case of pentacene films deposited for 15 min, flat and wide domains appeared only at increased substrate temperatures. The pentacene films deposited at 60 and 90 ºC were better ordered than at RT. A similar result was found for the pentacene films grown on hydrogen-terminated Si(111) surfaces.[13] When pentacene was deposited for 2 h, domains became larger along with increasing the substrate temperature. At 90 ºC, however, amount of the pentacene molecules on the substrate was smaller than at RT or 60 ºC due to the re-evaporation. Thus, the thickness of the grown film was thinner, and gaps among domains were wider. It was difficult to grow an enough thick pentacene film at 90 ºC in a reasonable deposition time.

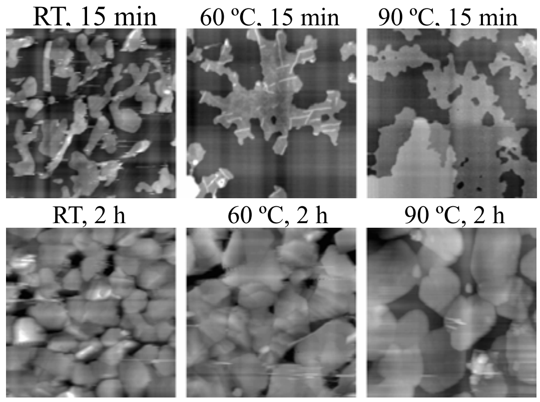

Figure 1. AFM images of pentacene films grown on the mica surfaces for various substrate temperatures and deposition times. All images show 2×2 μm^2 scan area.

Figure 2 shows XRD patterns of the pentacene films deposited on mica for various substrate temperatures. The XRD peaks from the pentacene films were labeled as (001) and (002), and indicated by dotted lines. Other large reflection peaks come from the mica substrate. According to the XRD patterns, the pentacene film deposited at RT consisted of a single phase, so called "thin-film" one that has the layer spacing of 1.53 nm. When the substrate temperature was raised to 60 ºC, the pentacene film consisted of a mixture of two phases, "thin-film" and "bulk" phases.[14] The latter corresponds to the layer spacing of 1.42 nm. In the case where the substrate temperature was 90 ºC, the pentacene film mainly consisted of the "bulk" phase. But every peak was smaller than RT or 60 ºC because of the thinner film thickness.

To investigate the crystal structure of pentacene films on the mica surfaces, we carried out RHEED measurement. After the growth of pentacene films with 0.6~1.2 nm thickness, the streak patterns coming from the mica substrate became dim. Thereafter, new streaks together with spots appeared for the films thicker than about 1.5 nm. These patterns were kept unchanged after the multilayer growth of pentacene. Similar streak patterns were also observed for other substrate temperatures. When pentacene was deposited on a thermally grown SiO_x, no streak pattern was observed. Therefore, the in-plane ordering of the pentacene film grown on the mica surface is supposed to be better than that on thermally grown SiO_x.

Figure 3 shows the drain-source current (I_D) versus drain-source voltage (V_D) characteristics of the pentacene OFET fabricated on mica at 60 ºC for the various gate-source voltage (V_G). Gate leak current was smaller than 1 nA even for the elevated gate voltage. The field-effect mobility (μ) was evaluated in the linear region using a following equation:

$$\frac{\partial I_D}{\partial V_G} = \frac{WC\mu}{L} V_D$$

where C is the capacitance per unit area of the gate dielectric; 3.5 nF·cm^{-2} for 1 μm thickness mica. On the mica gate, μ was 2.4 × 10^{-3} cm^2·V^{-1}·s^{-1} for the film grown at 60 ºC, while μ for the films grown at RT and 90 ºC were 4.6 × 10^{-4} cm^2·V^{-1}·s^{-1} and 2.6 × 10^{-4} cm^2·V^{-1}·s^{-1}, respectively. The on-off ratio and the threshold voltage (V_{th}) were best for the film grown at 60 ºC, and they were 11 and 88 V, respectively. In the case of OFET fabricated at RT, the pentacene film had smaller domains and more grain boundaries, and the film

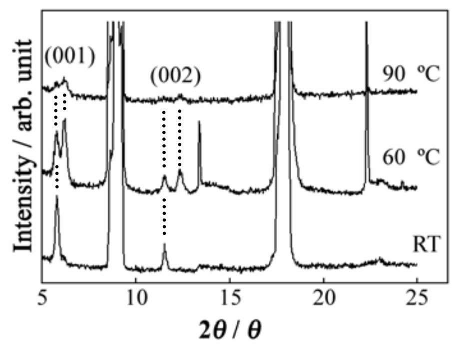

Figure 2. XRD patterns of pentacene films deposited on the mica surfaces for various substrate temperatures.

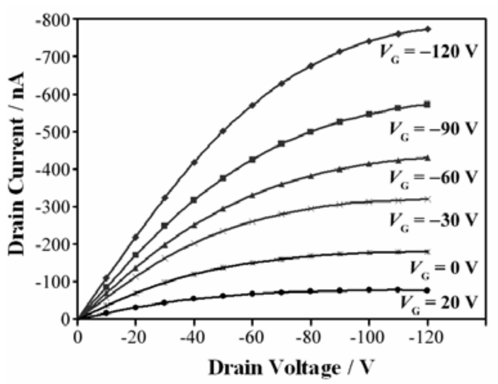

Figure 3. Drain-source current (I_D) versus drain-source voltage (V_D) characteristics of pentacene OFET fabricated on mica at 60 ºC for various gate-source voltage (V_G).

crystallinity was poor. The pentacene film grown at 90 ºC was too thin to show good OFET performance.

The mobility, on-off ratio and V_{th} of the pentacene OFET fabricated on the mica gate substrate were much worse than those on amorphous SiO_x.[1] We ascribe its poor performance to following reasons. First, the cleavage of mica might be incomplete so that its surface was rather rough, or some small irregular pieces of cleaved flakes remained between source and drain electrodes. Usually a narrow area of the cleaved mica surface is atomically smooth, but some defects or steps can exist in the wider channel region of OFET. Next, the Au gate electrode deposited on the backside of the mica substrate might be poorly attached to mica because of the inertness of the mica surface. In this case, injection of hole carriers into the pentacene layer will be reduced. These problems should be technically improved, which are currently under investigation. Another possibility is that randomly distributed potassium ions on the cleaved surface of mica might work as a positively charged scattering center for holes in the channel. This problem could be overcome by using another kind of layered silicate without cations on its cleaved surface.

4. Summary

We explored possibility of fabrication of OFETs on inexpensive and single-crystalline natural mica substrates. By observing the morphology and the ordering of pentacene films on the mica surfaces by XRD, AFM and RHEED, epitaxial growth of pentacene was confirmed. Typical FET characteristics were observed for the pentacene OFET on the mica gate dielectric although the mobility at the present stage was still low as compared with that on SiO_x.

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研究成果（2）関連

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