氏　　　　　　　　名	KIM Joonam
学 位 の 種 類	博士(マテリアルサイエンス)
学 位 記 番 号	博材第 418 号
学位授与年月日	平成 29 年 3 月 24 日
論 文 題 目	Investigation of solution process of molybdenum disulfide for thin film transistor applications
論 文 審 査 委 員	主査　徳光　永輔　北陸先端科学技術大学院大学　教授
	小矢野　幹夫　同　教授
	下田　達也　同　教授
	水田　博　同　教授
	上野　啓司　埼玉大学大学院理工学研究科　准教授

論文の内容の要旨

Introduction

The two dimensional (2D) materials such as graphene have attracted great attention because of high carrier mobility and outstanding mechanical property. However, the graphene has very small band-gap (< 0.7 eV)[1]. Although there is amount of work to make the band-gap for the graphene, it had been not working on. Meanwhile, other types of 2D material, transition metal dichalcogenide (TMDC) also shows great potential in nanoelectronics and optical application. In particular, atomically layered molybdenum disulfide (MoS_2) has attracted attention. When the thickness of MoS_2 is reduced from bulk to nanosheet, the bandgap (E_g) transforms from an indirect (E_g=1.2 eV) to a direct (E_g=1.8 eV)[2].

Recently, exfoliated single layer MoS_2 has been applied to transistor and excellent on/off current ratio with high carrier mobility was reported [3]. Nevertheless, most devices using the MoS_2 have been fabricated on small flake exfoliated from single crystals in order to investigate of fundamental properties. However, there are many restrictions such as small and uncontrollable flake size and extreme difficulty in the alignment for device fabrication so it limits their application in macroscopic scale devices. On the other hand, the chemical solution process is promising for large area formation of MoS_2 with simple equipment at low cost. However, there are a few researches about chemical solution processes for MoS_2 films. Moreover, almost MoS_2 synthesis is worked on the silicon dioxide (SiO_2) substrate because of thermal stability and flat surface of SiO_2 but deposited MoS_2 film have to be transferred to other substrate such as high-dielectric-constant (high-k) thin film because of low dielectric constant of SiO_2 for a device. However, during transfer the MoS_2 film, problems such as film wrinkle, chemical damage by etching solution of SiO_2 must come up.

In my work, fundamental properties of solution process of MoS_2 films on high-k thin film have been investigated. In particular, MoS_2 films were fabricated on high-k films for the purpose of thin film transistor (TFT) applications.

Research Purpose

The objective of this research is to develop chemical solution process for MoS_2 thin films and to apply the solution-derived MoS_2 to thin film transistors. To achieve the TFT applications, MoS_2 films are grown on high-dielectric-constant (high-k) materials directly by chemical solution process.

Results and Discussion

The $(NH_4)_2MoS_4$ dissolved in N-methyl-2-pyrrolidone (NMP) was used for a precursor of MoS_2. To obtain well defined MoS_2 film, the coating uniformity is important and it is strongly related to

the surface energy. In our work, the coating property for a precursor of MoS_2 was firstly investigated by a surface energy measurement. The estimated contact angles and calculated components of the oxide substrate are summarized in table 1. The oxide film which has relatively large γ- and small γ+ of surface energy, shows good coating property. Putz et al[4]. have suggested the solution structure of $(NH_4)_2MoS_4$ dissolved in solvent, there is the network linked via [RNH_2—H—NH_2R] cations, where the proton is stabilized via two NH_2 molecules, which may play an important role for coating properties. . If the substrate surface has a significant amount of positive ions, it becomes difficult to deposit the films because of the Coulomb repulsive force with cations. For Si, SiO_2 and PZT, the estimated γ+ values were relatively high. Hence, it is difficult for the $(NH_4)_2MoS_4$ solution to be spin-coated completely.

Table 1. Summary of the estimated contact angle of the test liquid, calculated surface energy components, coating state and film state annealed at 1000 °C with sulfur.

Substrate	Contact angle				γ_S^{LW}	γ_S^+	γ_S^-	γ_S	Coating state	Film state annealed at 1000 °C with sulfur
	water	diiodomethane	Ethylene glycol	glycerin						
Al_2O_3	33.8	38.9	32.7	-	40.2	0	54.1	40.4	good	good
HfO_2	24.8	32.6	21.7	-	41.9	0.08	65.3	46.5	good	poor
ZrO_2	9.7	34.2	-	15.6	42.4	0.07	64.5	46.6	good	good
$Pb(Zr,Ti)O_3$	31.4	27.1	-	38	45.4	0.47	41.6	54.2	poor	-
$(Bi,La)_4Ti_3O_{12}$	24.8	32.6	27	-	40.4	0.06	46.3	43.8	good	poor
LZO	23.5	28.7	1.0		44.7	0.065	54.4	48.5	good	-
NZO	34.3	35.4	19.9		41.8	0.1	47.0	47.3	good	good
ALZ	17.3	35	0.7		42.0	0.1	60.1	47.3	good	-
Si	59.7	48.8	38.1	-	35.0	0.43	22.3	41.2	poor	-
SiO_2	47	45.1	25.1	-	37.5	0.53	33.4	45.4	poor	-

To fabricate the MoS_2 thin film, two step annealing process (1^{st}:450 °C in Ar/H_2 atmosphere, 2^{nd}: 1000 °C in Ar/S atmosphere), was applied. Among high-k materials such as HfO_2, ZrO_2 and Ti O_2, ZrO_2 system was most stable for second thermal treatment process of MoS_2. In our work, the electric properties for Nb 30% doped ZrO_2 (NZO) which has higher dielectric constant than pure ZrO_2 with same degree of leakage current, was firstly reported.

Figure 1(a) shows the Raman spectra for the MoS_2 films fabricated by source solutions with various concentrations. Two Raman peaks, E_{2g} and A_{1g}, are observed in the Raman spectra for all films. The peak position difference, which is a good trace for the thickness estimation, is plotted in figure 1(b). The peak difference of the MoS_2 film fabricated by the 0.05 mol/kg solution corresponds to a thickness of over five layers. On the other hand, a thickness of three layers was estimated for the film grown by the 0.0125 mol/kg solution. When the source solution with a concentration of 0.00625 mol/kg was used, the thickness of the film is further decreased to two mono-layers, although the Raman peak intensity becomes small.

The thin film transistors (TFT) using solution processed MoS_2 as semiconductor which was directly deposited on the NZO as gate insulator, were fabricated with channel length of 10 μm and

width 50 μm, respectively as shown in figure 2(a). The 0.05 mol/kg MoS_2 solution was used so the width of Raman peak in figure 2(a) was 26 cm^{-1} (over five layers). The calculated filed effect mobility which was calculated from figure 2(b), was 0.32~0.71 cm^2/Vs. and the on/off ratio was $4.5x10^4$. This value is almost the same as that reported for TFT with transferred or CVD multilayer MoS_2

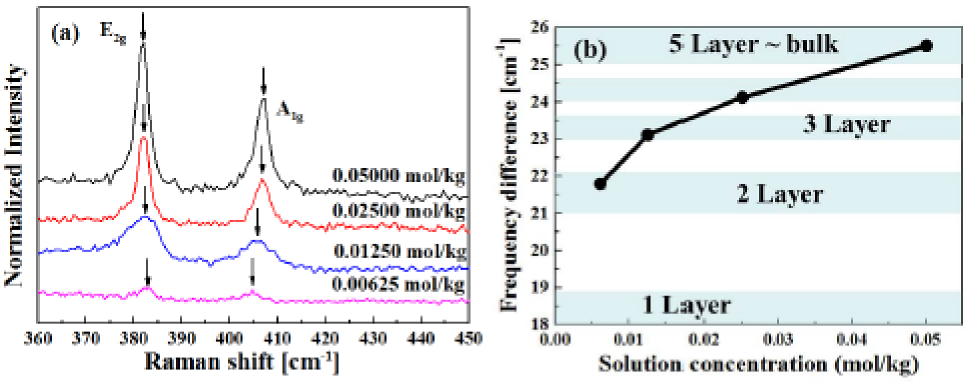

Figure 1. (a) Raman spectra of MoS_2 fabricated by source solutions with various concentrations. (b) Frequency difference between the peak of the E_{2g} and A_{1g} mode as a function of the concentration of the source solution.

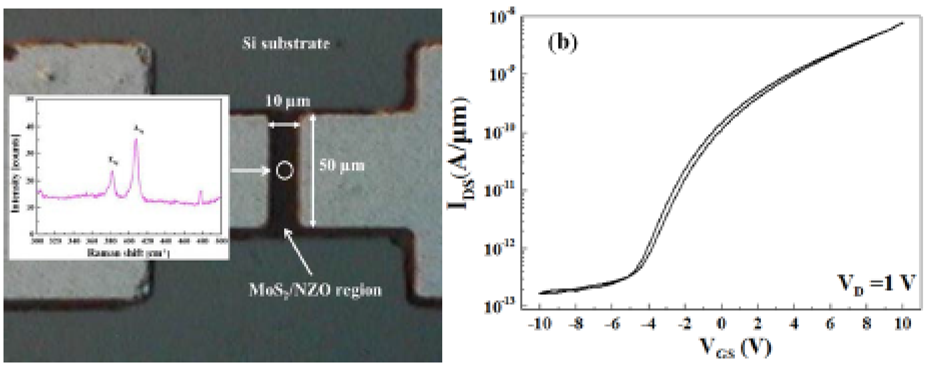

Figure 2(a) Plan view of metal pad for multilayer MoS_2 transistor and its Raman spectra, (b) the characteristic of (a)gate-voltage and drain current.

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Keywords: Solution process, High-k , MoS_2, semiconductor, TFT

論文審査の結果の要旨

シリコン集積回路の微細化の限界が見え始めた現在、電子移動度の大きいグラフェンなどの 2 次元材料が次世代エレクトロニクス用の新材料として期待されている。中でも MoS_2をはじめとする遷移金属カルコゲナイド 2 次元材料は、グラフェンとは異なりバンドギャップを持つ半導体であり、電子移動度も比較的大きいことから近年特に注目を集めている。これらの材料は、従来は単結晶片からの機械的剥離法、または気相成長法で一旦 SiO_2/Si 基板上へ成長した後に目的とする絶縁膜上へ転写する手法によりデバイス応用されていた。これに対し本研究では、安価で大面積に均一な成膜が可能な溶液プロセスに着目し、化学溶液法による MoS_2膜の形成技術を確立し、さらに高誘電率ゲート絶縁膜上に直接 MoS_2薄膜を成長して薄膜トランジスタ（TFT）を実現することを目的としている。

本研究では、原料溶液を調製するところから研究を開始し、最初に様々な高誘電率絶縁膜上への塗布特性を評価して、表面エネルギーの極性項を考慮することで塗布特性が説明できることを明らかにした。次に、TFT 実現のためには高温の MoS_2形成過程が必要であることから、硫黄雰囲気での高温アニールに対する安定性の良い ZrO_2系の材料をゲート絶縁膜として選択し、化学溶液プロセスにより ZrO_2に Nb を添加した Nb-Zr-O（NZO）薄膜を形成している。Nb を添加することで正方晶が得られ、ZrO_2よりも高い誘電率が得られることを初めて明らかにしている。次に NZO 上へ MoS_2原料溶液を塗布し、還元雰囲気での 450℃の 1 次アニールと、650～1000℃の硫黄雰囲気での 2 次アニールを施すことによって MoS_2層状構造の成長に成功したことを、ラマン分光法、X 線回折、X 線光電子分光法等により確認している。また透過型電子顕微鏡観察により、MoS_2の 2 次元構造が基板表面の凹凸に沿って基板に平行に成長していることを明らかにしている。さらに溶液の濃度により 2 分子層程度までの膜厚制御が可能なことを示している。NZO 上に成長した MoS_2膜のホール移動度は 25cm^2/Vs であった。最後に、NZO 絶縁膜上に溶液プロセスにより直接形成した MoS_2膜をチャネルとして TFT を作製し､真空処理を施すことによりオン・オフ比 10^5程度の良好な n チャネルのトランジスタ特性を観測している。化学溶液プロセスにより直接ゲート絶縁膜上に MoS_2を形成してトランジスタを実現したのは本研究が初めてである。

以上、本論文は、これまでほとんど検討されていなかった化学溶液プロセスによりMoS_2膜の形成に成功し、さらにゲート絶縁膜上へ直接MoS_2膜を形成して薄膜トランジスタを実現した独創性の高い研究であり、学術上、応用上双方の観点から極めて価値の高いものである。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。