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# Investigation of solution process of molybdenum disulfide for thin film transistor applications

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#### 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<sub>2</sub>) has attracted attention. When the thickness of MoS<sub>2</sub> is reduced from bulk to nanosheet, the bandgap (E<sub>g</sub>) transforms from an indirect (E<sub>g</sub>=1.2 eV) to a direct (E<sub>g</sub>=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<sub>2</sub>) substrate because of thermal stability and flat surface of SiO<sub>2</sub> but deposited  $MoS_2$  film have to be transferred to other substrate such as high-dielectric-constant (highk) thin film because of low dielectric constant of SiO<sub>2</sub> for a device. However, during transfer the  $MoS_2$  film, problems such as film wrinkle, chemical damage by etching solution of SiO<sub>2</sub> 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<sub>2</sub>. To obtain well defined MoS<sub>2</sub> 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  $\gamma$ - and small  $\gamma$ + 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<sub>2</sub> 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<sub>2</sub> and PZT, the estimated  $\gamma$ + values were relatively high. Hence, it is difficult for the  $(NH_4)_2MoS_4$  solution to be spin-coated completely.

Substrate	Contact angle							Coating	Film state annealed at	
	water	diiodomethane	Ethylene glycol	glycerin	γs <sup>LW</sup>	γs⁺	γs	γs	state	1000 °C with sulfur
Al <sub>2</sub> O <sub>3</sub>	33.8	38.9	32.7	-	40.2	0	54.1	40.4	good	good
HfO <sub>2</sub>	24.8	32.6	21.7	-	41.9	0.08	65.3	46.5	good	poor
ZrO <sub>2</sub>	9.7	34.2	-	15.6	42.4	0.07	64.5	46.6	good	good
Pb(Zr,Ti)O <sub>3</sub>	31.4	27.1	-	38	45.4	0.47	41.6	54.2	poor	-
(Bi,La) <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>	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 <sub>2</sub>	47	45.1	25.1	-	37.5	0.53	33.4	45.4	poor	-

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.

To fabricate the MoS<sub>2</sub> thin film, two step annealing process ( $1^{st}$ :450 °C in Ar/H<sub>2</sub> atmosphere,  $2^{nd}$ : 1000 °C in Ar/S atmosphere), was applied. Among high-k materials such as HfO<sub>2</sub>, ZrO<sub>2</sub> and Ti O<sub>2</sub>, ZrO<sub>2</sub> system was most stable for second thermal treatment process of MoS<sub>2</sub>. In our work, the electric properties for Nb 30% doped ZrO<sub>2</sub> (NZO) which has higher dielectric constant than pure ZrO<sub>2</sub> 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  $\mu$ m and

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



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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