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# 중합 박막 트랜지스터를 위한 Ta<sub>2</sub>O<sub>5</sub> 유전체 접합의 자기조립 단분자막의 특성

(Characteristics of Self assembled Monolayer as Ta<sub>2</sub>O<sub>5</sub> Dielectric Interface for Polymer TFTs)

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## 요 약

중합 박막 트랜지스터의 특성은 유기 반도체에 앞서 게이트유전체 표면의 화학적 변형에 의해 조절 가능하다. 화학적 처리는 자기조립 단분자막 형태의 유전물질과 함께 과생된 tantalum pentoxide(Ta<sub>2</sub>O<sub>5</sub>) 표면으로 구성된다. Octadecyl trichlorosilane(OTS), hexamethyldisilazane (HMDS), aminopropyltrethoxysilane(ATS) 자기조립 단분자막의 성장은 중합체로 결합된 poly-3-hexylthiophene (P3HT)의 분위기에서 0.01 ~ 0.06 cm<sup>2</sup>/V·s의 이동도로 진행되었다. 이동도 향상 메커니즘은 중합체와 자기조립 단분자막 사이의 분자 상호작용에 영향을 미치는 것으로 확인하였다. 이는 향후 polymer TFT의 유전박막 중 하나로서 유용하게 사용 될 것이다.

## Abstract

The characteristics of polymeric thin-film transistors(TFTs) can be controlled by chemically modifying the surface of the gate dielectric prior to the organic semiconductor. The chemical treatment consists of derivative the tantalum pentoxide(Ta<sub>2</sub>O<sub>5</sub>) surface with organic materials to form self-assembled monolayer(SAM). The deposition of an octadecyl-trichlorosilane(OTS), hexamethyldisilazane(HMDS), aminopropyltrethoxysilane(ATS) SAM leads to a mobility of 0.01 ~ 0.06 cm<sup>2</sup>/V·s in a poly-3-hexylthiophene(P3HT) conjugated polymer. The mobility enhancement mechanism is likely to involve molecular interactions between the polymer and SAM. These result can be used for polymer TFT's dielectric material.

**Keywords** : Ta<sub>2</sub>O<sub>5</sub>, polymer TFT, dielectric, poly-3-hexylthiophene(P3HT)

## I. Introduction

The interest in spontaneously organized molecular assemblies, such as self-assembled monolayer

(SAM), has born itself into many disciplines of engineering including lubrication, biotechnology, catalysis, and microelectronics. sheer diversity of the potential applications renders the study of these assemblies critical to the advancement of science and technology. Technologies utilize the potential of the monolayer to contract and expand depending upon temperature in order to create a molecular "gate". Of great interest to the whole scientific community is the ability of SAM to foster a deeper scientific understanding of interfacial and interphase behavior at the atomic level. The success of solution processed

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polymers as semiconducting materials in TFTs depends critically on achieving high field-effect carrier mobilities. The room temperature carrier mobility of organic polymers has improved steadily in the past fifteen years, from  $10^{-5} \sim 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$ <sup>[1]</sup>. Molecularly ordered films lead to higher mobilities. The highest mobility  $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$  has been achieved in TFTs having region-regular P3HT as the semiconductor<sup>[2]</sup>.

Optical spectroscopy and x-ray diffraction suggest that the high mobility is due to  $\pi$ - $\pi$  stacking in the polymer film, giving rise to two-dimensional charge transport<sup>[2]</sup>. The carrier mobility is higher in oriented films along the rubbing direction than in isotropic films and can be as high as  $0.02 \text{ cm}^2/\text{V}\cdot\text{s}$  at room temperature<sup>[3, 4]</sup>. It is suggested that the mobility anisotropy is caused by the longer intrachain carrier diffusion length when the polymer backbone is parallel to the channel length.

## II. Experiment

TFT performance depends largely on the semiconductor/dielectric interface<sup>[5]</sup>. The purpose of this work is to show that improved characteristics of P3HT-based TFTs are obtained by controlling the chemistry of the dielectric/polymer interface. We chose to use thermal Ta<sub>2</sub>O<sub>5</sub> as the dielectric because of its well-characterized properties and ease of chemical modification. Derivative the dielectric surface with self-assembled monolayers(SAMs) prior to the deposition of the semiconductor leads to the highest reported carrier mobility in the unoriented phase. TFT devices were fabricated in the staggered top contact geometry in order to minimize contact resistance<sup>[6]</sup>. The gate electrode was Tantalum(Ta) 150nm by RF-sputtering and gate dielectric layer was Ta<sub>2</sub>O<sub>5</sub> with anodically method. Prior to the deposition of the polymer, the substrates were immersed in different organic trichlorosilane solution (20 mM in hexadecane or heptane) to form a monolayer on the surface of the oxide<sup>[7]</sup>. The trichlorosilanes investigated in this

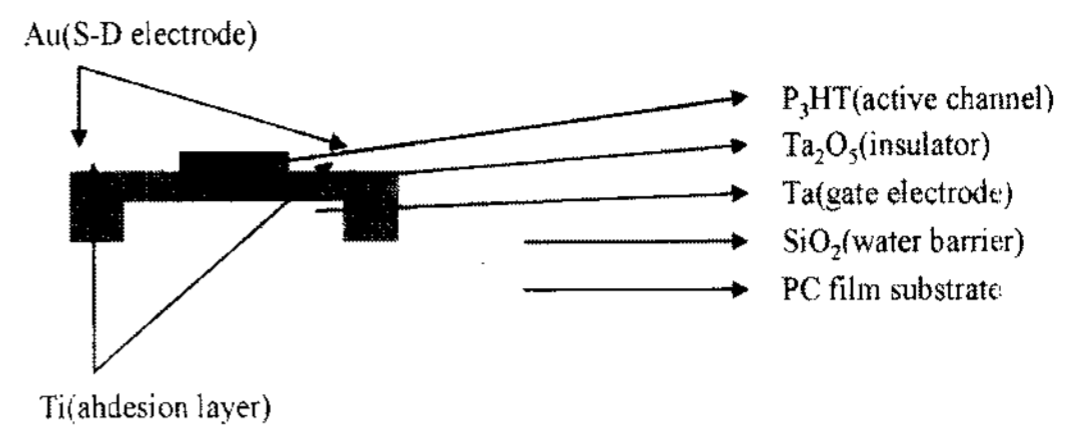


그림 1. OTFT 에서 활성층과 같은 역할을 하는 P3HT의 위치와 그 구조

Fig. 1. Structure of a organic thin-film transistor(OTFT) with poly-3-hexylthiophene semiconductor as an active layer.

work are OTS with -CH<sub>3</sub> end groups, ATS with -NH<sub>2</sub> end groups and HMDS with -OH end groups as silane coupling agent. After treatment, the oxide surface was characterized by measuring a 0.2 wt% P3HT solution in chloroform. OTS, ATS and HMDS were method by dipping and P3HT films were spin-coated. Source and drain gold contact were thermally evaporated. The P3HT TFTs reported here use a bottom electrode fabricated on plastic substrates as shown Fig. 1.

## III. Results and discussion

The effect of dielectric surface treatment on carrier mobility in the polymer is still not well understood. Siringhaus et al.<sup>[8]</sup> observed that replacing siloxyl groups on the Ta<sub>2</sub>O<sub>5</sub> surface with methyl groups by treating the dielectric with HMDS leads to a mobility increase in P3HT. The increase was attributed to the presence of apolar groups at the surface leading to phase segregation of the polymer at the interface<sup>[8]</sup>. This mechanism is not consistent with the mobility increase observed on OTS-treated surfaces. If the mobility depended only the presence of methyl groups on the devices fabricated on the HMDS-treated surface would have characteristics to those fabricated on the OTS-treated surface. Moreover, a similar enhancement in mobility after treating the dielectric surface with OTS is observed in vapor-deposited polycrystalline pentacene films<sup>[9]</sup>. The carrier mobility in the polymer does not depend monotonically on the surface energy of the dielectric, as would have been

표 1. 각 trichlorosilane 에 따른 Tr의 특성값  
Table 1. Transistor parameters extracted from transfer curves of TFTs deposited on dielectric surface.

	Mobility (cm <sup>2</sup> /Vs)	Ion/Ioff	RMS (nm)
No treatment	0.005 ~ 0.008	10 <sup>3</sup> ~ 10 <sup>4</sup>	31~34
HMDS	0.01 ~ 0.03	10 <sup>3</sup> ~ 10 <sup>4</sup>	20~25
OTS	0.04 ~ 0.06	10 <sup>3</sup> ~ 10 <sup>4</sup>	41~44
ATS	0.008~ 0.01	10 <sup>3</sup> ~ 10 <sup>4</sup>	48~52

expected if the mobility was governed only by contamination adsorbed at the dielectric surface<sup>[6]</sup>. Moreover, the HMDS-treated surface has a lower energy than the ATS-treated and OTS-treated surface. Table I indicated that the mobility increase is specific to certain SAM structures and is not simply related to macroscopic quantities such as polarity or surface energy.

The SAMs that provide the best results have long alkane chains(OTS), which allow them to interact with similar features in the structure of P3HT via induced-dipole dispersion forces<sup>[10]</sup>. The alkane chains in OTS, amino chain in ATS and hydroxyl chains in HMDS extend perpendicularly to the Ta<sub>2</sub>O<sub>5</sub> surface. The mobility enhancement cannot be caused by inplane alignment of the polymer backbone. Indeed, no long-range order is revealed by cross-polarized microscopy. Moreover, in-plane order cannot occur at the microscopic scale either, as the SAMs do not have any in-plane preferential orientation, and the orientation of the contacts on the film is random. On the other hand, both interlocking of the alkane chain of P3HT and OTS, as well as stacking of the amino chain of P3HT against those of ATS and hydroxyl chain of P3HT against those of HMDS, would cause a preferential out-of plane orientation of the amino chain and hydroxyl chain in the polymer, which would effectively improved the  $\pi$ - $\pi$  stacking in the direction of current flow and lead to higher mobility. Fig. 2. show that I-V electrical characteristics of each trichlorosilane.

In fact, by the AFM observation of the

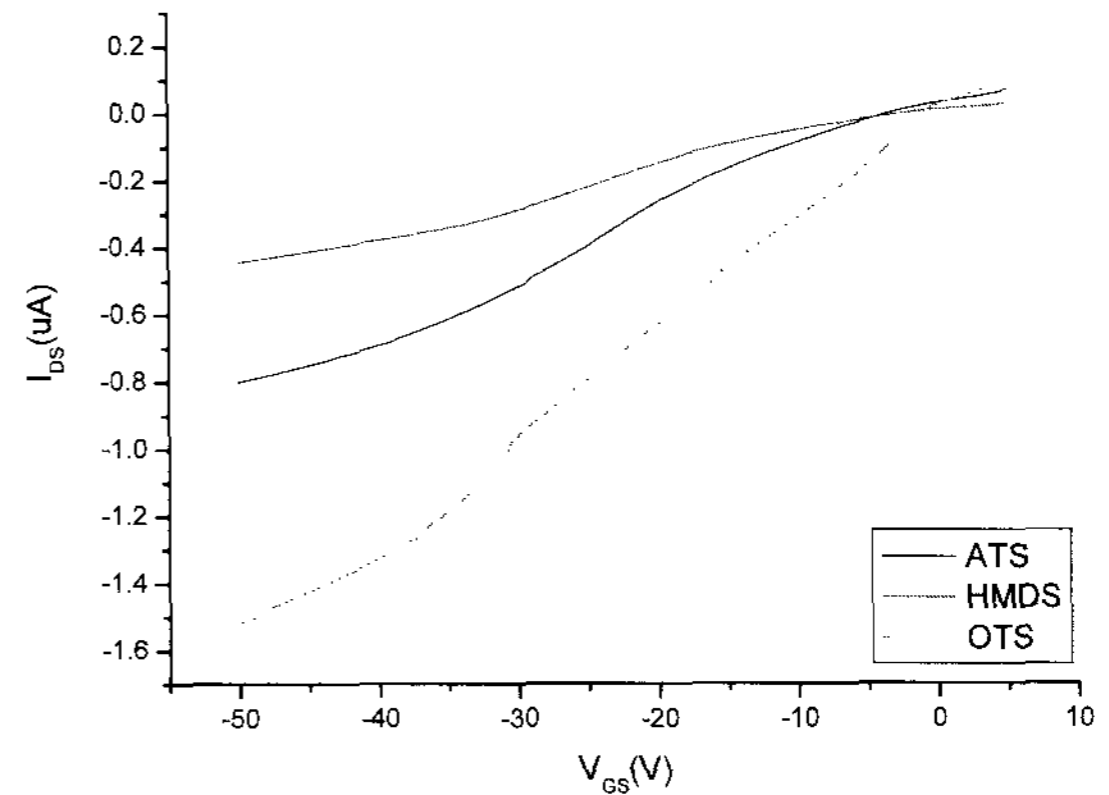


그림 2(a). 각 trichlorosilane 에 따른 I<sub>DS</sub>-V<sub>GS</sub> 특성 곡선  
Fig. 2(a). I<sub>DS</sub>-V<sub>GS</sub> characteristics of each trichlorosilane.

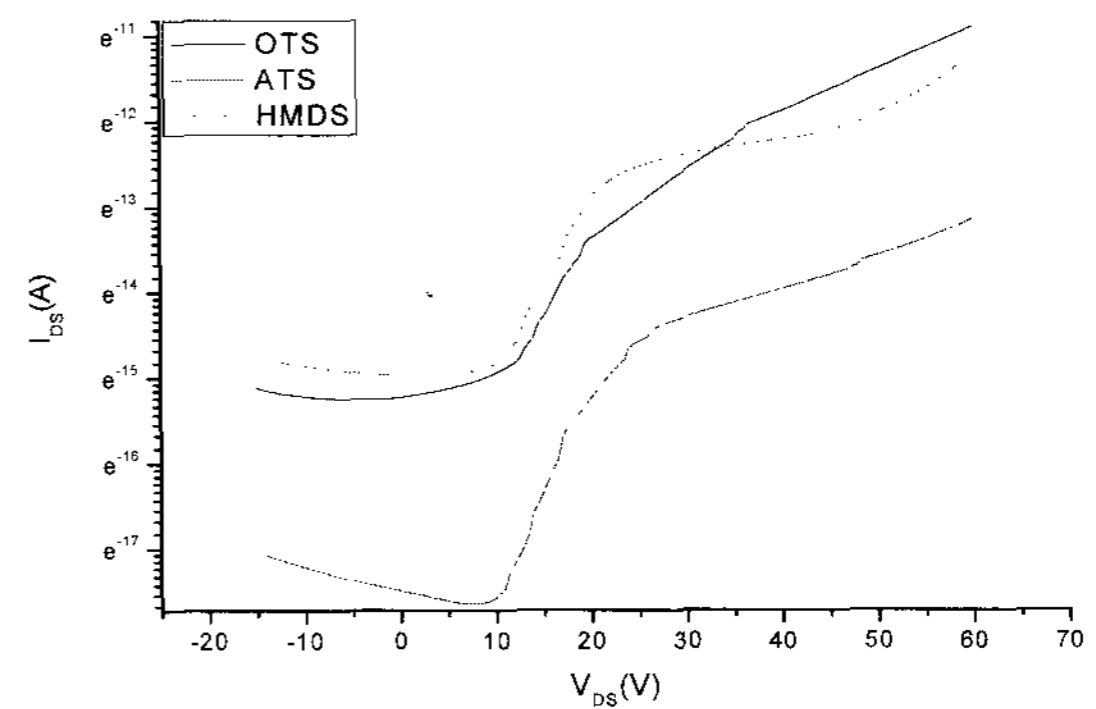


그림 2(b). 각 trichlorosilane 에 따른 I<sub>DS</sub>-V<sub>DS</sub> 특성 곡선  
Fig. 2(b). I<sub>DS</sub>-V<sub>DS</sub> characteristics of each trichlorosilane.

trichlorosilane solution (20 mM in hexadecane or heptane)treated a monolayer on the surface of the oxide. We can observe the improvement of the surface roughness by a factor of 20~25 as shown in Fig. 3. The increased mobility in the HMDS treated device, OTS treated device, and ATS treated device, can be explained by the changes of the insulator /semiconductor interface states correlated with the surface roughness of the insulator. The RMS factor in OTS treatment is 20~25 nm, but other is higher than OTS treatment. Table 1 show a detail value in AFM factor.

#### IV. Conclusion

In conclusion, chemically modifying the Ta<sub>2</sub>O<sub>5</sub>/

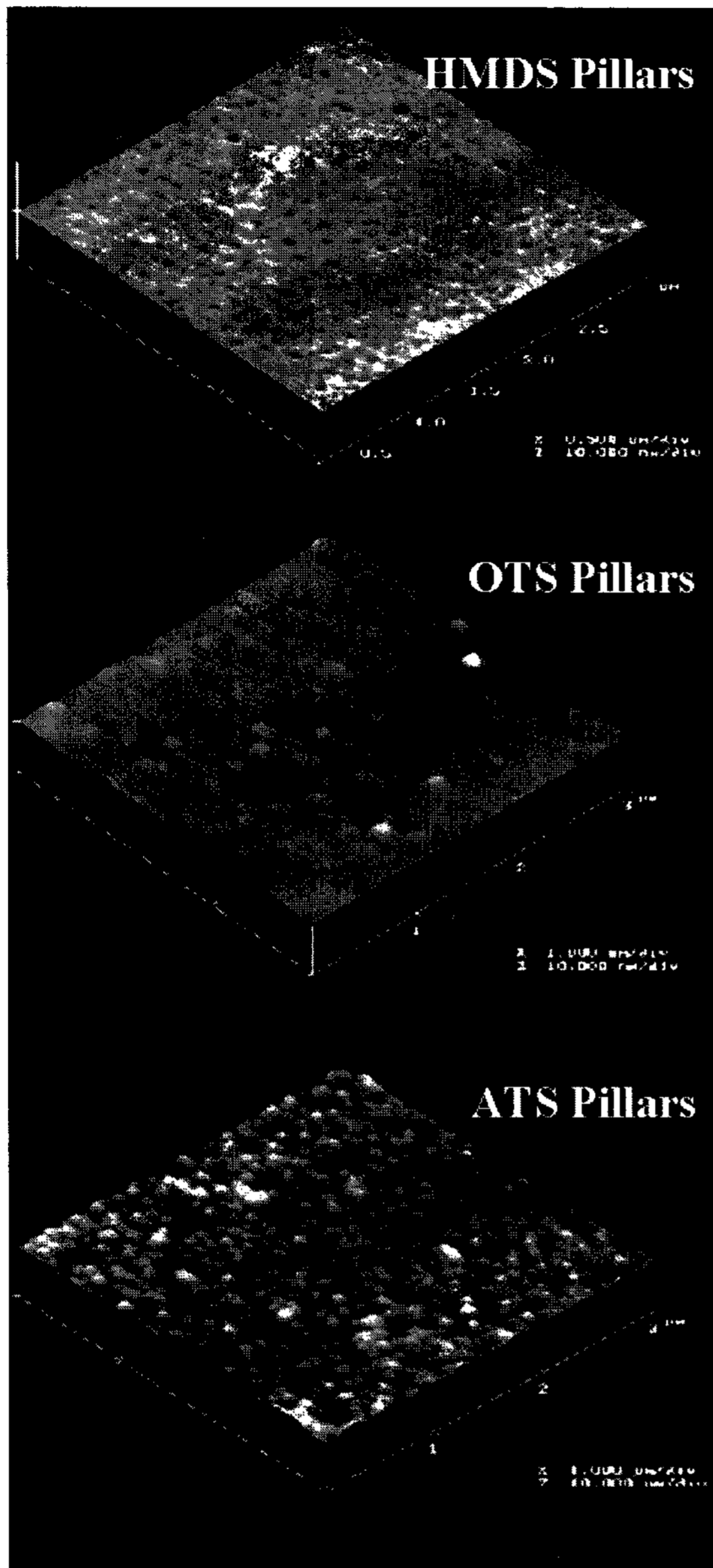


그림 3. 각 trichlorosilane 용액 처리후의 표면 단분자막 사진 : (a) HMDS 처리, (b) OTS 처리, (c) ATS 처리

Fig. 3. AFM image of the trichlorosilane solution treated a monolayer on the surface of the oxide. : (a) HMDS treatment, (b) OTS treatment, (c) ATS treatment.

polymer interface with SAMs allows the enhancement of carrier mobility in spin-casted P3HT. The highest mobility is obtained by treating the dielectric with OTS and is similar to the highest reported mobility of oriented P3HT. In contrast, with the latter, the films deposited on OTS-treated Ta<sub>2</sub>O<sub>5</sub> do not require deposition on a rubbed polymeric alignment layer and a high-temperature anneal. The mobility enhancement

mechanism is different than phase P3HT and is likely to involve molecular interactions between the SAMs and the polymer.

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