Atomic Hydrogen Annealing of Gate Dielectric in Pentacene Organic Thin-Film Transistors

Akira HEYA ^{a,*}, Masahiko SATO ^a, Hiroshi HASEGAWA ^a and Naoto MATSUO ^a

^aDepartment of Materials Science and Chemistry, University of Hyogo(2167, Shosha, Himeji-shi, Hyogo 671-2280)

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1. Introduction

Recently, performance of organic thin-film transistors (OTFTs) has improved. The carrier mobility of pentacene TFT is now comparable to that of amorphous silicon thin-film transistors (TFTs) ¹⁾. Therefore, it is expected that OTFTs are applicable for use in special applications such as flexible displays and IC tags. The carrier mobility of pentacene TFT depends on the pentacene crystallinity, grain size, and interface properties between the pentacene film and gate insulator because grain boundary scattering, interface roughness scattering, and surface scattering affect the mobility. Therefore, a pentacene film with a large grain and a smooth interface is necessary to improve the carrier mobility.

The grain size and the crystallinity of pentacene film depend on the surface state of the gate insulator. For that reason, the surface energy affects the grain size of the pentacene film and OTFT characteristics. Therefore, various surface treatments using dry and wet processes were investigated to improve the crystallinity of pentacene film and OTFT characteristics ^{2)~4)}. Plasma treatments using H₂, O₂, and NH₃ gases are known as methods for improvement of TFT characteristics for dry processing ⁵⁾. However, plasma treatments risk damage to electrical devices because of the use of electrical power. Additionally, it is difficult to treat large areas simultaneously.

We have developed a low-temperature surface treatment, named atomic hydrogen annealing (AHA) ⁶⁾. Using this method, hydrogen molecules are decomposed by catalytic cracking reactions on a heated catalyzer placed near the substrate. The sample surface is heated using recombination energy from atomic hydrogens to molecules and it is reduced. This method is useful to treat a sample with a large area simply by spreading the catalyzer widely without incurring plasma damage. The decomposition efficiency of H₂ is much higher on a heated catalyzer surface than in the gas phase, as in the case of a plasma process ⁷⁾.

In this study, the AHA process was applied to improve the electrical characteristics of pentacene OTFT. The effects of AHA on film properties and electrical characteristics of OTFT were investigated.

2. Experimental

For this study, Si wafers ((111), n-type, 100-mm diameter, 500 μm thick and 0.2-0.4 Ω cm) were used. Each Si wafer was cleaned using SH solution (H₂SO₄ : H₂O₂ = 1 : 3) at 100 °C for 600 s. A 350-nm-thick SiO₂ film was formed by thermal oxidation

using a mixture of O₂ and H₂O moisture at 1000 °C for 1800 s. The AHA apparatus is presented schematically in Fig. 1. A tungsten wire of 0.4 mm diameter and 400 mm length was used as a catalyzer. The flow rate of H₂ (purity 99.9999 %) and gas pressure were, respectively, 100 sccm and 30 Pa. The catalyzer temperature (*T*_{cat}) and the treatment time were, respectively, 1500 °C and 1800 s. The maximum substrate temperature was 110 °C.

The change in surface morphology induced by AHA was investigated using contact-mode atomic force microscopy (AFM). The chemical bond states of the SiO₂ surface with and without AHA were examined using X-ray photoelectron spectroscopy (XPS). The XPS profiles were obtained using an Al Kα X-ray of 400 μm diameter and a neutralization gun. The wide spectra and narrow spectra (Si2p and O1s) were measured respectively at three days and at sixty days after air exposure. The surface properties of samples were evaluated from the contact angle of a water droplet (1.5 μl).

The pentacene films were deposited by vacuum thermal evaporation five days after AHA treatment. However, the SiO₂/Si substrate subjected to AHA was kept in a vacuum desiccator until pentacene deposition. The pentacene film deposition was conducted until 1 hr after air exposure. After air exposure, the Au source and drain electrodes were deposited on the pentacene/SiO₂/Si substrate by electron beam (EB) evaporation, but it was feared that the interface between pentacene and Au films was degraded by O₂ and H₂O in air. The OTFT pattern was fabricated using a metal-shadow mask.

Fig. 1 Schematic diagram of AHA apparatus. The SiO₂/Si substrate was treated using a chemical reaction and the recombination energy of atomic hydrogen generated by catalytic cracking reactions on a heated catalyzer.

* E-mail: heya@eng.u-hyogo.ac.jp

The sample-holder temperature was RT and base pressure was lower than 2×10^{-4} Pa. The respective thicknesses of pentacene and Au films were 50 and 300 nm. The channel length and width of OTFT were, respectively, 1 and 10 mm. Electrical characteristics of pentacene OTFT were evaluated at RT in air. The carrier mobility (μ) was estimated from the linear region of I_D - V_D characteristic by assuming that the carrier transport was band conductivity.

3. Results and discussion

The AHA slightly decreased the intensity ratio of O1s to Si2p (O/Si ratio) in XPS wide spectra. The full width at half maximum (FWHM) of Si2p and O1s were slightly decreased respectively from 1.96 to 1.91 eV and from 1.76 to 1.72 eV by AHA. The FWHM of the XPS peak for SiO₂ surface relates to crystallinity. Results show that the SiO₂ adopted a stable structure by removal of a weak bond in SiO₂ network by atomic hydrogen. In addition, the peak positions of Si2p and O1s were changed, respectively from 104.1 eV to 103.6 eV and from 532.7 eV to 533.0 eV by AHA. Reportedly, the peak attributable to O-Si at 530.9 eV is a trap site of the carrier⁸. Apparently, the peak at 530.9 eV was decreased by AHA.

The surface properties of SiO₂ with and without AHA are presented in **Table 1**. The refractive index was decreased slightly from 1.46 to 1.45. The contact angle of a water droplet on the SiO₂/Si substrate was increased from 64° to 73° by AHA, which implies that the decrease in refractive index was related to reduction of the

SiO₂ surface. The AFM image shows that the surface roughness (Ra) of SiO₂/Si substrates with and without AHA was not changed by AHA. The decrease in grain size by surface roughness⁹ and degradation of OTFT characteristics by interface scattering are negligible. Results show that the surface state of SiO₂ can be modified by AHA without an increase in surface roughness.

The dendritic grain was observed in AFM images of pentacene films. The respective grain sizes of pentacene with and without AHA were 0.46 and 0.41 μ m. The grain size was increased slightly because the surface energy was decreased by AHA.

Fig. 2 shows I_D - V_G and $\sqrt{I_D}$ - V_G characteristics of the pentacene OTFTs. The respective mobility values of OTFT with and without AHA were 0.042 and 0.051 cm²/Vs. The value of V_{th} decreased from 65 to 16 V and that of $I_{on/off}$ improved from 10 to 100 by AHA. Reportedly, silanols (Si-OH) exist on the SiO₂ surface and have negative charge¹⁰. In addition, a dangling bond exists at the interface between the SiO₂ film and Si substrate, which indicates that negative charges exist on the SiO₂ film and at the interface of the SiO₂ and Si substrate. In this case, the channel was formed without application of the gate voltage. Consequently, the V_{th} and off current was high and the $I_{on/off}$ were very low for OTFT fabricated without AHA. Contact angle measurements show that the SiO₂ surface hydrophobicity was increased by AHA. This result implies that the hydroxyl group on the surface is removable using atomic hydrogen. Additionally, atomic hydrogen passivates and de-passivates Si dangling bonds at the Si (111)/SiO₂ interface via the reactions $P_b + H^0 \rightarrow P_bH$ and $P_bH + H^0 \rightarrow P_b + H_2$ ¹¹. It is considered that AHA has an effect of removal of negative charges on SiO₂ film and at the interface between SiO₂ and the Si substrate.

4. Conclusions

The pentacene film grain size was not increased drastically by AHA, although the surface energy of SiO₂ film was changed from 42 to 39 dyne/cm by AHA. However, V_{th} was decreased from 65 to 16 V and the on/off ratio was improved from 10 to 100 by AHA. The effect of AHA is related to the removal of negative charges on SiO₂ films and the interface of SiO₂/Si substrate by atomic hydrogen. Results obtained in this study demonstrate that AHA is a promising technique for improving OTFT characteristics.

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Table 1 Surface properties of SiO₂ with and without AHA.

	Without	With AHA
Ra roughness (nm)	0.15	0.13
Film thickness (nm)	360	363
Refractive index	1.46	1.45
XPS intensity ratio of O1s/Si2p	5.58	5.41
FWHM of Si2p peak (°)	1.96	1.91
Contact angle of droplet (°)	64	73
E_s (dyne/cm)	42	39

Surface energy (E_s) was estimated from the contact angle.

Fig. 2 I_D - V_G and $\sqrt{I_D}$ - V_G characteristics of the pentacene OTFTs with and without AHA. The value of V_D was -30 V. The V_{th} was estimated from $\sqrt{I_D}$ - V_G characteristics.