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## Molecular Crystals and Liquid Crystals

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### A Scanning Tunneling Spectroscopy Study on TCNQ/n-Si and/p-Si

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## A Scanning Tunneling Spectroscopy Study on TCNQ/n-Si and/p-Si

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A thin film (thickness: 1.5 nm) of tetracyanoquinodimethane (TCNQ), a well-known electron acceptor, was fabricated on p-Si and n-Si using a spin casting method. The junction properties of these systems were investigated using scanning tunneling spectroscopy (STS). I/V curves of the two systems showed rectifying properties with different polarity. It can provide a new technology to fabricate molecular-level rectifier if nanolithography is accomplished on these systems.

**Keywords** TCNQ; Spin-coated film; AFM lithography; rectifier.

### INTRODUCTION

The ultimate goal of nanotechnology is to fabricate nano-sized devices using an individual molecule after Aviram and Ratner proposed a molecular rectifier.<sup>1</sup> Several fascinating methods have been developed to achieve this goal mainly using based on an asymmetric molecular junction between molecules and molecules.<sup>2-4</sup>

In this study a new method is designed to fabricate a molecular-level rectifier using the heterojunction between an organic molecule and inorganic Si. A traditional method to make a solid-state rectifier is to use a combination of p-doped Si and n-doped Si. If a p-type semiconductor is regarded as an electron acceptor, an organic electron acceptor may replace a p-type inorganic semiconductor. Tetracyanoquinodimethane (TCNQ, Figure 1) was selected as an electron acceptor. As TCNQ has 8  $\pi$ -electrons, each molecule tends to accept two

electrons from the environment so that the Hückel theorem can be satisfied. A spin casting method is used to fabricate a junction of TCNQ and p- type or n-type Si due to its simplicity and easiness. The I/V property between TCNQ and p-doped or n-doped Si will be measured using scanning tunneling spectroscopy.

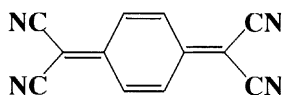


FIGURE 1. Structure of TCNQ

## EXPERIMENTAL

For a practical application, the TCNQ film was fabricated by a spin casting method. 0.01 g of TCNQ (Aldrich, USA) solution in hexane was prepared and filtered through a 0.2  $\mu$ m membrane filter. The TCNQ film was fabricated on a Si wafer at the speed of 3000 rpm for 30 seconds and heated at 100 °C for 1 minute in order to vaporize residual solvent using a spin coater. An n-type (14~23  $\Omega$  cm) or a p-type (7~25  $\Omega$  cm) Si wafers (Siltron Inc., Korea) was chosen for investigation whether the junction properties of electron acceptor/n-Si or p-Si will affect the lithographic results. Before used as a substrate, 1 cm x 1 cm of Si wafer was cleaned in a 1:3 solution of 30% H<sub>2</sub>O<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> at room temperature for 30 minutes and rinsed with deionized water (Milli-Q reagent grade 18 M $\Omega$  cm, Millipore Co., USA) for 10 minutes.

The thickness and roughness of the spin-coated film were characterized using an AutoEl II null-type ellipsometer (Rudolph Technology Inc., USA) and an AFM (Digital Instruments Inc., USA), respectively.

All scanning tunneling spectroscopy (STS) experiments were performed under an air-operated STM system (DI, USA). An STM tip was prepared by a mechanically cutting Pt/Ir (80/20) wire without an etching process. During STS measurements, all feedback was opened with adjusting tip bias voltage and tunneling current to be 0.5 ~ 2.0 V, 1.5 nA for TCNQ /n-Si and -0.5 ~ -2.0 V, -1.5 nA for TCNQ/p-Si, respectively.

## RESULTS AND DISCUSSION

$1.5 \pm 0.2$  nm of TCNQ thin film was fabricated on p-doped or n-doped Si. The uniformity of the film was confirmed using AFM.

Figure 3 exhibits an I/V curve of doped Si only. Regardless of dopant

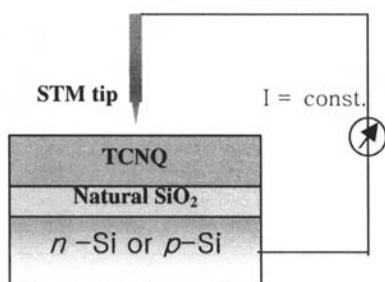


Figure 2. Scheme of STS

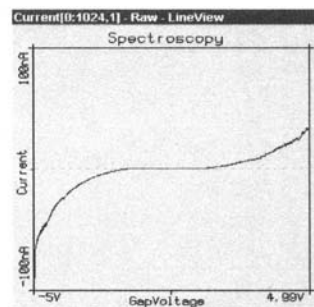


Figure 3. I/V of  $\text{SiO}_2/\text{Si}$

type, this nonlinearity was commonly measured. No current was measured between  $-1$  V and  $1$  V. Figures 4 and 5 present I/V curves of TCNQ/n-Si and TCNQ/p-Si, respectively. The I/V curves of the two systems were dramatically changed to reveal a rectifying property. The presence of only  $1.5$  nm TCNQ film altered I/V curves of the two systems dramatically. Even though there exists  $1$  nm thick natural  $\text{SiO}_2$  layer, it can be regarded as a potential barrier which only limits current flowing through the system. The role of silicone oxide as a barrier is also found in other molecular-level device.<sup>3</sup>

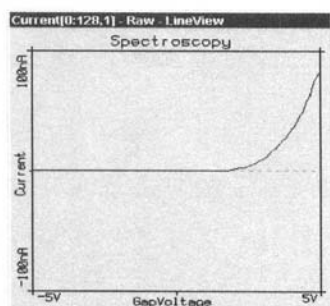


Figure 4. I/V of TCNQ/ $\text{SiO}_2$ / n-Si

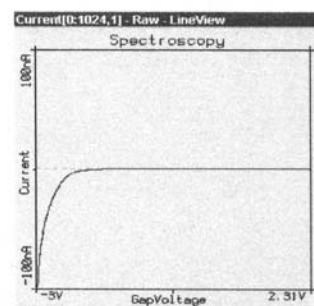


Figure 5. I/V of TCNQ/ $\text{SiO}_2$ / p-Si

Further detail study has been carrying out for elucidation on mechanism of a rectifying property shown in the junction between an organic acceptor and n-/p-Si. The I/V data shown in Figures 3, 4, and 5 were confirmed by STS measurements at more than 10 different places with different tips.

For a fabrication process, AFM anodization lithography can be applied to this system.<sup>6</sup> It is expected that nano-sized patterning by the lithography enable us to make 50 nm x 50 nm rectifying units directly. Since TCNQ is a good electron acceptor, this active resist will reduce the starting voltage and widen the voltage range for the lithography.

## CONCLUSIONS

We designed a methodology to build a nano-sized rectifier using a junction between organic molecules and a Si substrate. The rectifying property of the system was confirmed by STS. The application of AFM lithography to the system enables us to practically fabricate 50 nm x 50 nm rectifiers.

## ACKNOWLEDGMENT

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