

# Wednesday Morning Poster Sessions

## Organic Films and Devices

### Room: Exhibit Hall B2 - Session OF+EL-WeP

## Organic Films and Devices

### OF+EL-WeP1 Cycloaddition of Silyl-disila-cyclopentene on Si(001) Surface, *B.-Y. Choi, Y.-J. Song, Y. Kuk*, Seoul National University, South Korea

It is known that  $\pi$  bonds of unsaturated organic molecules can easily react with Si=Si dimers of the reconstructed Si(001)-2x1 surface, resulting in two new Si-C  $\sigma$  bonds. Through such a cycloaddition, densely-packed molecules on hybridized Si(001) surface are highly ordered both translationally and rotationally over macroscopic length scale. However, in spite of much effort, the mechanism of cycloaddition on surface is not known clearly. We investigated the reaction of 2-silyl-1,3-disilacyclopent-4-ene (SDC) with the Si(001) surface using scanning tunneling microscopy. STM images show that the SDC molecules are slightly elongated parallel to the dimer direction, suggesting that the molecules bond in a manner of typical [2+2] cycloaddition. It can be noted that there exists a preferred bonding site of SDC molecule. However, the analysis of the observed structure suggests that there is more than one way for SDC to bond to the Si(001) surface. Some molecules place perpendicular to dimer direction and even complex absorbates are shown. We suggest that the several reactions occur nearly as frequently.

### OF+EL-WeP2 Nanolithography Technique Based on Dynamic Mode Atomic Force Microscopy and Organosilane Self-Assembled Monolayers, *K. Hayashi, N. Saito, H. Sugimura, O. Takai*, Nagoya University, Japan

Organosilane self-assembled monolayer (SAM) is a candidate for resist material in future nanolithography techniques. Although several techniques have been applied to patterning of the SAMs, scanning probe lithography using an atomic force microscope (AFM) is promising since the method has a high potential in achieving nanometer scale resolution. However, there has been a serious problem, that is, damages of the AFM-tip, when the AFM is operated in the contact mode. Here we report on nanopatterning of organosilane SAMs using a dynamic mode AFM in which tip damages are expected to be reduced. We observe AFM-tip induced chemical changes on the SAM surfaces by Kelvin-probe force microscopy (KFM) working in the dynamic mode as well. Onto cleaned silicon (Si) substrates covered with native oxide ( $\text{SiO}_2$ ), a SAM was formed from n-octadecyltrimethoxysilane [ODS:  $\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{OCH}_3)_3$ ]. Thickness of this ODS-SAM was ca. 1.8 nm. While scanning a AFM-tip (Au coated Si tip), operated in the dynamic mode, on an ODS-SAM/Si sample, a DC bias voltage was applied between the conductive tip and the sample. After the patterning, the sample surface was characterized by KFM. Due to electrochemical reactions induced by the injected current, the modified region where current had been injected from the tip was found to show a more positive surface potential than the surrounding unmodified region. Through the surface potential images acquired by KFM, chemical changes of ODS-SAM could be detected, while such changes could hardly be confirmed in topographic images. KFM is a powerful means to characterize nanoscale patterns on the SAMs drawn by scanning probe lithography.

### OF+EL-WeP3 Photoemission Study of Dodecanthiol on Au (111), *H. Geisler, S. Sales*, Xavier University of Louisiana, *J.M. Burst, S.N. Thornburg, C.A. Ventrice Jr.*, University of New Orleans, *Y. Losovyj, P.T. Sprunger*, Louisiana State University

The adsorption of alkanethiols on various single-crystal metal surfaces results in the formation of self-assembled monolayers (SAMs). Typically, SAMs are grown on surfaces that are immersed in aqueous solutions, and adsorption times of 15 hours or more are necessary to obtain well-ordered, defect free structures. In this study, 1-dodecanethiol was vapor deposited on Au (111) in ultra high vacuum, which produces a SAM in a period of only a few minutes. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) was used to determine the orientation and the electronic structure of the thiol. Deposition at room temperature gave no signature of thiol adsorption at the surface with either ARUPS or low energy electron diffraction (LEED). Deposition at  $\sim 100$  K resulted in an ordered monolayer, as indicated by the dispersion of the thiol valence band emissions. A comparison between clean gold and the SAM spectra indicate that the 1-dodecanethiol adsorbs upright at a  $20^\circ$  angle to the surface normal. Deposition of multilayers of thiol at  $\sim 100$  K produced a disordered overlayer with no dispersion of the valence band emissions. The onset of

emission from the thiol valence band for the multilayer films was measured to be 3.5 eV below the Fermi level.

### OF+EL-WeP4 XPS Studies of Brilliant Green Doped Conducting Polymer Polythiophene Films, *H.K. Kato, S.T. Takemura, M.H. Hirayama*, Kanto Gakuin University, Japan, *H.M. Makiyara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule brilliant green (BG) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between the dye molecule and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that BG molecules were injected into polymer matrix in the hybrid films prepared by electrochemically reduced method and BG diffused method. S 2p lines were observed split indicates simultaneous doping of BG cation and  $\text{HSO}_4^-$ . The higher binding energy peak corresponds to  $\text{HSO}_4^-$  while lower binding energy peak can be assigned to the S sites of polymer backbone. Synthesized film samples were categorized into two types, A-type and B-type by the difference of S 2p core-level energy shift. In the sample of A-type, the energy shift of the lower peak of S 2p suggest the charge transfer between BG molecules and polymer backbone creating a n-type polymer backbone state. In the case of electrochemically as-grown films, both BG and  $\text{HSO}_4^-$  doping were not observed because S 2p line was single and no N 1s signal was observed.

### OF+EL-WeP5 XPS Studies of Initial Stage of Conducting Polymer Film Growth on Si Substrate, *H.K. Kato, S.T. Takemura*, Kanto Gakuin University, Japan, *H.M. Makiyara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) film growth on Si substrate was investigated by XPS. PT/Si interface fabricated by electrochemical method was closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. At the initial stage of electrochemical polymer growth, affinity between a deposited polymer PT film and Si substrate was strong compared with the case of PT film growth on ITO substrate expecting bondings between polymer chains and Si substrate layers. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different Gaussian components correspond to different valence states of Si in contrast to the core-level spectra of non-deposited Si substrate. The lower binding energy peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Strong affinity between a deposited polymer PT film and Si substrate and variation of the XPS spectral profile suggest that Si-C and Si-F bondings are created at the PT/Si interface.

### OF+EL-WeP6 Formation and Characterization of Ferrocene and Porphyrin Monolayers on Si and Ge Surfaces : Towards a Hybrid Molecular/CMOS Electronic Device, *A. Yasseri, Z. Liu, R. Dabke*, University of California Riverside, *V. Malinovskii, K.H. Schweikart, J.S. Lindsey*, North Carolina State University, *W.G. Kuhr, D.F. Bocian, K.M. Roth*, University of California Riverside

Construction of a novel hybrid molecular based device may provide the most tractable approach in bridging the gap between modern day semiconductor materials and molecular based devices. Toward this goal, we have examined functionalized monolayers of ferrocene and porphyrin terminated alcohols and thiols covalently linked to mono-crystalline Si and Ge (100) and (111). Electrochemical communication with the surface immobilized molecules was achieved through a covalently anchored Si-O, Si-S or Ge-O and Ge-S tether to photolithographically patterned surfaces. Silicon microelectrodes were fabricated on heavily doped silicon masked with a thermally grown oxide to define the active electrode area for monolayer assembly. Surfaces were activated via a two-step process. Chemically stable hydride-terminated surfaces, using HF or ammonium fluoride, were reacted with a solution of iodine yielding an iodide functionalized surface. XPS measurements confirm the mechanism for the displacement of surface iodine atoms via a base catalyzed reaction with alcohol terminated iron and zinc-centered ferrocene and porphyrin respectively. Iodide derivitization prior to film deposition chemically facilitates the formation of more densely packed monolayer of porphyrins. Fast scan voltammetry performed on monolayers demonstrate the chemical stability of the films over millions of cycles in an inert atmosphere.

Modified AC voltammetry was used to probe the redox kinetics of the semiconductor film junction in order to measure the rate for film oxidation and reduction under an applied potential. Monolayers formed from solution phase assembly reactions were further characterized using scanning probe microscopy.

**OF+EL-WeP7 Characterization of OLED Degradation by Emission Microscope, N. Miura, Y. Luo, K. Takagi, ITES Co. Ltd., Japan**

The purpose of this study is to investigate how an emission microscope has been applied to evaluation for the degradation mechanism of organic light-emitting devices (OLED). One of the most effective ways to characterize OLED degradation is to study a physical and chemical phenomenon that occurs with an exact point of interest. The problem, however, is one of isolating the exact point of degradation. Thickness of a luminescent layer is around 0.1 microns. Consequently, a less-than-0.1-micron foreign matter can become a cause of an electrical short failure. On the other hand, a size of a pixel is the approximately one hundred microns. Therefore pinpoint detection of a failure location is extremely difficult. In order to solve this problem, an emission microscope used for a failure analysis of Si-based LSIs has been applied to detect a degradation point in plane luminescent devices. An emission microscope is a tool to detect a faint light emitting at a failure point with PMT or CCD camera and to find out a point of interest by adding an optical image and a detected one. This study describes a method for applying emission microscope in the failure analysis of OLED and demonstrates the effectiveness of this method. It is confirmed that an observation under sub-threshold bias condition is effective to find out a failure point. Although no electro-luminescence is observed under this condition with an optical microscope, an emission microscope can get detect a photon emission at a failure location. Some case studies are described to demonstrate the effectiveness of this method. Cross sectional TEM observations of defects located with this technique are also included.

**OF+EL-WeP8 Polyatomic Ion Deposition of Thiophenic Thin Films, Y. Choi, E.R. Fuoco, L. Hanley, University of Illinois at Chicago**

Oligo- and polythiophenes are utilized as conducting polymers in many applications. Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces.<sup>1</sup> We demonstrate here the growth of thiophenic thin films on aluminum and silicon substrates by mass-selected <200 eV C<sub>4</sub>H<sub>5</sub>S<sup>+</sup> ion beams. Thiophenic films are also grown by non-mass selected ion beams containing <200 eV C<sub>4</sub>H<sub>5</sub>S<sup>+</sup> and fragment ions. Our non-mass selected ion deposition method permits rapid film growth over wide substrate areas and it is described here for the first time. X-ray photoelectron spectroscopy and atomic force microscopy are used to compare the film chemistry and morphology for the two methods. Oxidation of the films during aging in air is observed.

<sup>1</sup>L. Hanley and S.B. Sinnott, Surf. Sci. 500 (2002) 500.

**OF+EL-WeP9 Mg-Phthalocyanine Thin Films with High Sensitivity for Chlorine Gas, T. Miyata, S. Kawaguchi, T. Minami, Kanazawa Institute of Technology, Japan**

There has been considerable interest in the study of organic substances such as phthalocyanines in thin film form for use as the active layer in gas sensor devices. In particular, the electronic properties of metal phthalocyanine (MPc) thin films are known to be affected by the presence of a foreign gas. Recently, we have demonstrated newly developed high-sensitivity chlorine (Cl<sub>2</sub>) gas sensors using Cu-phthalocyanine (CuPc) thin films. However, these CuPc thin film gas sensors still have several unsolved problems such as low sensitivity at operating temperatures above 150°C and the necessity of a heat treatment process for repeated operation. In this paper, we introduce newly developed chlorine gas sensors that can be operated at high temperatures using Mg-phthalocyanine (MgPc) thin films. The Mg-phthalocyanine thin films (thickness from 30 to 180 nm) were evaporated onto substrates; Au thin films were deposited as electrodes. The substrate temperature was varied from RT to 180°C. Gas sensitivity is defined as ratio (I-I<sub>0</sub>)/I<sub>0</sub>. Here, I<sub>0</sub> and I are the currents through the sensors before and after gas introduction, respectively. The sensor resistance decreased when exposed to chlorine gas; MgPc thin film gas sensors exhibited high sensitivity at the operating temperatures as high as 230°C. The characteristics of MgPc thin film sensors were strongly dependent on the preparation conditions of the MgPc thin films. For example, sensitivity increased as the substrate temperature of the MgPc thin films was increased from RT to 180°C: maximum sensitivity at a thin film deposition temperature of 180°C. At an operating temperature of 200°C, the sensitivity of the optimized MgPc thin film gas sensor linearly increased with the Cl<sub>2</sub> gas concentration in the range of 0.35 to 35 ppm.

**OF+EL-WeP10 The Surface Stress under Ion Irradiation on Si and SAM-coated Si, A.N. Itakura, M. Kitajima, Institute for Materials Science, Japan, R. Berger, IBM Deutschland Speichersysteme GmbH, Germany**

Evaluation of stress in the Si stencil mask is very important for ion projection patterning or ion lithography technology, because the stresses would cause a deformation of the projected patterns. Ar ion irradiation makes a compressive stress on Si(001) surfaces.<sup>1</sup> Stencil masks often become folded during the ion projection patternings, which should be owing to this ion induced compressive stress. In this paper, we have studied the stress evolution of Si membranes under ion irradiation. Bare Si and alkanethiol-coated-Si were examined during ion irradiation from ion energies of 5 to 50eV. The stresses were in-situ real-time monitored by using a microcantilever sensor technique combined with ion irradiation system in UHV. Self-assembled monolayers (SAM) such as alkanethiol, HS-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>3</sub> for n=4,6,8,12, on gold induced compressive stresses.<sup>2</sup> In contrast to the compressive stress during SAM growth, a strong tensile surface stress of about -0.7 N/m was found when the sensor is exposed to Ar ions. This value is 3-4 times larger than the compressive stress. The constant value of the tensile stress for an Ar-ion dose higher than 4 x 10<sup>14</sup> ions/cm<sup>2</sup> indicates that a stable monolayer forms during Ar-ion irradiation. Stable protective monolayers featuring tensile stress can play a key role in micro-machining and as protective overlayers for silicon mask lithography.

<sup>1</sup>T.Narushima, A.N.Itakura and M.Kitajima, Appl.Phys.Lett.79, 605-607 (2001),

<sup>2</sup>A.N.Itakura, R.Berger, T.Narushima and M.Kitajima, Appl.Phys.Lett.(2002), in printing.

**OF+EL-WeP11 Controlled Growth of Ultrathin Molecular Films, E.J. Kintzel, Jr., Florida State University, D.-M. Smilgies, Cornell High Energy Synchrotron Source, Cornell University, J.G. Skofronick, S.A. Safran, D.H. Van Winkle, Florida State University**

Controlled growth of the aromatic p-phenylene oligomer molecules adsorbed onto KBr(001), KCl(001), NaCl(001), and NaF(001), has been investigated by x-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis provides evidence that the substrate temperature during deposition, substrate lattice constant, and molecular length affects the molecular orientations within these ultrathin films. AFM images contribute independent evidence for a surface microstructure evolution that is consistent with the XRD results. Oriented films can therefore be grown with the desired molecular orientations by careful selection of an appropriate combination of the above deposition parameters.

**OF+EL-WeP12 Current Sensing AFM Study on Electric Property of Organic Monolayer Formed on Hydrogen Terminated Si(111) via Si-C Bond, K. Uosaki, J.-W. Zhao, Hokkaido University, Japan**

Current Sensing AFM was used to measure the conductivity of alkyl monolayer of various chain length formed on hydrogen terminated Si(111) via Si-C Bond. Conductance was dependent on chain length, bias and force. The current increased exponentially with the bias. Based on the chain length dependence of the Log(current) - bias relation, the conduction mechanism is discussed. The force dependence of the conductance at a given bias was well explained by the bending of the monolayer and the chain length dependence of the mechanical property of the monolayer will be discussed.

**OF+EL-WeP13 Surface Structure and Surface Properties of Organosilane Monolayers Selectively Assembled on the Si-wafer Substrate, A. Takahara, T. Koga, M. Morita, H. Otsuka, Kyushu University, Japan**

Three-component micropatterned organosilane monolayers were successfully fabricated on Si-wafer substrate by stepwise vacuum ultraviolet-ray (VUV) photolithography technique with a rotation of line-type photomask. The introduction of different organosilanes was confirmed by X-ray photoelectron spectroscopy (XPS). Atomic force microscopic and lateral force microscopic observations revealed that the line-widths of micropatterned surface corresponded to those of photomask. Micropatterning of the surface functional groups influenced the magnitudes of surface free energy.

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