

Nanomanufacturing Science and Technology Focus

Topic

Room: East Exhibit Hall - Session NM-TuP

Nanomanufacturing Science and Technology Poster

Session

NM-TuP1 Nanoscopic Polymerization of Polyaniline on the Nanostructured Alumina Surface and the Nano-Contact Transfer of the Nanofabricated Polyanil. *Y. Watanabe, T. Mori, H. Kato, S. Takemura, T. Hiramatsu*, Kanto Gakuin University, Japan

The aim of the present study is to present what types of nano-size structures and patterns made of polyaniline can be created in local polymerization in nanoscopic area such as nano-size crater or trench. The authors also intend that the fabricated polyaniline patterns can be transferred to other substrate such as silicon wafer by a nano-contact method. Nanoscopic polymerization of polyaniline was conducted locally in nanoscale craters or highly-oriented line pattern with nanoscale trenches fabricated on an aluminum surfaces by combined process of chemical treatments and anodization. Nanoscopic polymerization process was performed by a wet method. Aniline monomer solved in pure water, which was added by oxidation agent ammonium peroxodisulfate (APS) solved in HCl in a test tube, was dropped on the nanostructures as a droplet with a micropipett and was extended on the surface. Aniline monomer was being polymerized in a test tube under those conditions. As for the linked-crater structure, the size of the crater ranged from 50 nm to 100 nm by dynamic force microscopy (DFM) measurements. On the other hand, as for the highly-oriented line structure, the line distance was estimated at 30-40 nm. Nanoscopic polymerization was conducted on the two types of nanostructured templates. DFM observation and the cross section analysis were conducted on pre-deposited and deposited surfaces. For the nanoscale polymerization on the linked-crater structure, one of the characteristic patterns was a polyaniline dots pattern. The DFM image showed that each crater was filled with polyaniline creating polyaniline dots. It was also found that binding small dots formed a tree-like network made of polyaniline covering the linked-crater surface. In the case of lower concentration of APS, dots became smaller. Preliminary stage of nanowire growth was also observed. On the other hand, as for the nanoscale polymerization on the highly-oriented line structure, one of the characteristic patterns was polyaniline line pattern where polyaniline polymerized in each trenches. At the next stage, nano-contact transfer of the fabricated polyaniline patterns to Si wafers was tried. In the case of the line pattern template, it was found that a polyaniline line pattern could be transferred to a Si wafer for the lower concentration of aniline monomer. It was also confirmed that the transferred pattern was changed into dots pattern for the higher concentration of aniline. By atomic force microscopy-current imaging tunneling spectroscopy (AFM-CITS) measurements, the obtained IV characteristics indicated the gap became broaden on the transferred polyaniline pattern.

NM-TuP2 Dielectric Performance of Post Deposition Treated Al₂O₃ Films Prepared by Using Parallel-Plate Electrode PEALD. *C.C. Yu*, National Applied Research Laboratories, Taiwan, Republic of China, *H.D. Trinh*, National Chiao Tung University, Taiwan, Republic of China, *B.H. Liu, C.C. Kei, C.N. Hsiao, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

In this study, self established plasma enhanced atomic layer deposition system (PEALD) was successfully used to deposit Al₂O₃ films at room temperature. Trimethylaluminum (TMAI) and ionized oxygen ions have used as metal precursors and oxidant, respectively. PEALD cycles comprised TMA pulsing and O₂ plasma treatment steps, and all the steps followed by purging nitrogen gas for 5 second. Parallel electrodes and DC power supply have applied to ignite O₂ plasma during ALD cycles. Effects of plasma power output have investigated by preparing Al₂O₃ films with different O₂ plasma power ranged from 7 – 50 W. Film thickness measurement has been carried out by using x-ray reflection analysis (XRR), and self limiting behavior has been investigated which verified PEALD growth mechanism. Growth rate of PEALD Al₂O₃ films that analyzed by XRR was ranged from 0.8 – 1.7 Å/cyc. Microstructure analysis of PEALD Al₂O₃ films have been characterized by using scanning electron microscope (SEM) and transmittance electron microscope (TEM) and revealed pin-hole free structures with excellent interfaces between films and substrates. Results of atomic force microscope (AFM) measurement show that PEALD cycle number varied from 100 – 500 cycles would lead to the smooth surface roughness of films ranged from 0.184 – 0.35 nm. Dielectric behavior of high-k capacitors has measured by using HP4284A LCR

impedance analyzer. The relations between D_{it} values and plasma power output have characterized and evaluated. The results of C-V measurement show shifted C-V curves and hint that the films deposited with different plasma power lead to varied D_{it} values. This phenomenon implies that higher plasma power causes higher amount of interfacial charge traps on the substrate surface. To study the effects of interfacial conditions on performances of capacitors, post treatment has been used to modify the film properties. Post deposition annealing technique has been applied by using rapid thermal annealing furnace (RTA). The adopted annealing temperatures were ranged from 300 – 500 °C for 30 seconds in nitrogen atmosphere. Improvements of Shifted C-V curves were investigated and carried out the varied D_{it} values as 10⁹ – 10¹⁸ / cm² - eV.

Key : PEALD, Direct plasma, High-k material, C-V, I-V, D_{it}, Parallel electrode

NM-TuP3 Effect of Growth Temperature on Optical Properties of TiO₂ Films by Atomic Layer Deposition. *M.H. Chan, C.C. Kei, C.N. Hsiao, W.-H. Cho, C.C. Yu, B.H. Liu, W.C. Chen, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

Titanium dioxide (TiO₂) films were deposited on Si and B270 glass substrates by a horizontal-flow atomic layer deposition (ALD) system. Titanium tetrachloride and deionized water were used as metal precursor and oxidant, respectively. Precursors were separately introduced into the reactor for a pulse length of 40 ms, and the working pressure was kept at 1 torr. Deposition temperature of TiO₂ films was varied between 100 and 300°C. Absorption coefficient and refractive index were obtained by using spectroscopic ellipsometry. Crystal structure of TiO₂ films was acquired by using X-ray diffractometry. Film thickness was obtained by scanning electron microscopy. Curve-fittings of ellipsometric data was also applied to evaluate the film thickness and growth rate of TiO₂ films. It was found that the crystallinity of Rutile TiO₂ films was significantly improved as increase the processing temperature from 150 to 300 °C. This might be the reason for an increasing refractive index of TiO₂ films prepared at a higher temperature. Beside, increase of precursors' reactive rate would result in a lower absorption coefficient for samples prepared at a higher temperature. The growth rate of TiO₂ film prepared at various temperatures is around 0.6 Å/cycle. However, a slight decrease in the growth rate can be observed due to the faster desorption rate of precursors at higher temperatures.

NM-TuP4 Fabrication of Double Nanohoneycombs (Pt/ZnO) with Controllable Size using Nanosphere Lithography and Plasma Enhanced Atomic Layer Deposition. *C.-T. Lee, W.-H. Cho, B.H. Liu, C.C. Kei, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

The double nanohoneycombs (Pt/ZnO) on glass and Si substrates were fabricated by nanosphere lithography (NSL) and plasma enhanced atomic layer deposition (PEALD). The first nanohoneycomb (ZnO) was fabricated by controllable size with NSL and magnetron sputtering. In this study, platinum thin films were deposited on ZnO nanohoneycomb by using PEALD using MeCpPtMe₃ and oxygen plasma as precursors. The effects of the thickness of platinum thin films on the structural and optical properties of the double nanohoneycombs (Pt/ZnO) were investigated by field emission scanning electron microscopy, X-ray diffraction and spectrometer. X-ray diffraction analysis revealed that the platinum thin films are polycrystalline with a preferred orientation along (111). This technique forming double nanohoneycombs, especially with desired period, is expected to be a candidate for wide nanostructure applications such as field emission, sensors, etc.

NM-TuP7 Fabrication of Nanopattern Sapphire Substrate by Nanosphere and Nanoimprint Lithography Technology. *C.M. Chang, M.H. Shiao, D.Y. Chiang*, National Applied Research Laboratories, Taiwan, Republic of China, *C.T. Yang*, Industrial Technology Research Institute, Taiwan, Republic of China, *M.J. Huang*, National Applied Research Laboratories, Taiwan, Republic of China, *W.J. Hsueh*, National Taiwan University, Taiwan, Republic of China

In this study, nanosphere lithography (NSL) and nanoimprint lithography (NIL) methods were used to fabricate metal pit and polymer pillar etching masks for sapphire substrate etching process, respectively. The metal mask contains 500 nm hole array and polymer pillar array mask which each pillar's size was 350 nm in diameter and height. Then inductively-coupled-plasma reactive ion etching (ICP-RIE) technique was used to etch sapphire substrate, which introduced both boron trichloride (BCl₃) and Argon (Ar) mixture etchant gases with 1 : 6 flow rate ratio. After etching processes were finished, two types of nanopattern structure were obtained on the sapphire substrate surface. One type of sapphire substrate was nano-pit array structure with 400 nm in diameter and 200 nm in depth, another type

of sapphire substrate was nano-cone array structure with 400 nm diameter and 100 nm in thickness. The contact angles of two patterned sapphire substrates were measured to be 101.02° and 98.14° for nano-pit array and nano-cone array structure, respectively. From the contact angle measurement results, it can be found that the surface property of sapphire substrate changed from hydrophilic, which contact angle was 24.46°, to be hydrophobic.

NM-TuP8 Fabrication of Single-Electron Transistor Utilizing Multi-Coated Self-Assembled Monolayer, N. Kwon, K. Kim, I. Chung, Sungkyunkwan Univ., Republic of Korea

We have fabricated quantum dots with the precise sizes from 30 nm to sub-10 nm at the controllable position. First, Au electrodes with the unique shape were obtained using a conventional lithography. Then, self-assembled multilayers, composed of alternating layers of α , ω -mercaptoalkanoic acids (~2 nm) and copper (II) ions, were deposited on Au electrode patterns to form the controllable gap between adjacent Au electrodes. After reaching to nanometer-scale gap, the second Au was deposited again. Finally, lift-off both e-beam resist and molecular resist were removed by lift-off, thereby resulting in quantum dot with nano-gap between gold electrodes. The physical properties were analyzed using scanning probe microscopy (SPM) and field emission scanning electron microscopy (FE-SEM). The electrical properties were evaluated using Keithley-4200.

NM-TuP9 Photoluminescence Studies of Nanostructured Alumina Surfaces Coated by Polythiophene Film and Copper Phthalocyanine, A. Ishii, R. Nakashima, H. Kato, S. Takemura, H. Kobe, Y. Watanabe, T. Hiramatsu, Kanto Gakuin University, Japan

Photoluminescent properties of the nanostructured alumina surfaces and the surfaces coated by polythiophene (PT) nanofilm and Copper phthalocyanine (CuPc) were investigated. Nanostructures such as linked-crater structure and highly-oriented line structure were prepared on an Al surface by a combined process of chemical and electrochemical treatments. The nanoscale linked crater structure was fabricated on an Al surface by treatment with Semi Clean and successive electrochemical anodization in H₂SO₄ solution created a nanoscale finer linked-crater structure on the surface. The crater size was estimated at 80-150 nm in diameter by dynamic force microscopy (DFM) measurements. Regarding the highly-oriented line structure, the anodization process applied to the original fiber-like surface structure on the Al plate. The anodization fabricated the finer line structure on the Al surface. The line distance was estimated at 40 nm. The fabricated nanostructured surfaces were identified as alumina by Fourier transform infrared spectroscopy (FT-IR) and x-ray photoemission spectroscopy (XPS) measurements. Conducting polymer polythiophene nanofilm growth on the nanostructured Al surface was conducted by an electrochemical synthetic method in an electrochemical cell. Polythiophene nanofilm was polymerized on the nanostructured Al used as an anode in acetonitrile containing thiophene monomer and (Et)₄NBF₄ by applying positive voltage to the anode. It was observed by DFM that nanofilm was grown along the crater structures or the line structures. CuPc deposition on the nanostructured surfaces was carried out by casting method. Photoluminescent properties of the nanostructured alumina surfaces and the surfaces topped by the nanofilm and CuPc were investigated. It was shown that characteristic ripples of several emission peaks appeared in the wavelength range of 350-550 nm in both cases of linked-crater and highly-oriented line structures while no ripple-shaped emission peaks were observed in the case of the original native Al oxide surface. The emission spectral profile was different in peak positions, number of ripples and intensities between two types of nanostructures. Photoluminescence measurements on the polythiophene nanofilm-grown linked-crater structure also showed that the rippled emission peaks clearly appeared. It was also clearly confirmed that the observed rippled emission patterns were significantly enhanced in both cases of CuPc deposited and nanofilm-coated nanostructures. The mechanism of generation of the rippled peaks and the enhancement were discussed by considering nanosize effects and Al-O vibration modes.

NM-TuP11 Optimization of Criss-Cross Photolithography for 3D NAND, J. Germain, J. Smith, J.M. Kim, K.Y. Ko, Applied Materials, Inc.

The patterning of small contact holes is an ever present challenge in the field of photolithography. Recently, the importance of this challenge has expanded both because of the development of 3D NAND architectures such as BiCS and because of the need to pattern even smaller contact holes for DRAM applications.

As the required critical dimensions and pitches of contact holes become smaller, the methods typically used for lithography become insufficient. One approach to solving this problem is the use of criss-cross lithography. In criss-cross lithography, two sets of lines are patterned perpendicular to each other, and a freeze step is used to bind them in place. In the first

portion of this work, criss-cross lithography is used to pattern 60 nm holes, with an argon freeze applied to harden the first layer of polymer before patterning the second layer. In this application, two types of problems were discovered: underexposure which causes patterns to become unstable due to gaps at the bottom of the structure and non-optimized dosing which results in patterns which, while circular before etch, exhibit X/Y directionality when any of a wide range of etch processes is applied to the pattern. We explain the causes of these two problems and demonstrate a consistent relationship between etch depth and X/Y directionality for these types of patterns.

In the later portion of this work we demonstrate the applicability of an alternate technique, thermal freeze, to the patterning of 60 nm contact holes. This technique has been applied and optimized such that it enables the criss-cross patterning approach to produce patterns that are consistent and circular even after the etch process. Along with demonstrating that thermal freeze can be used to produce criss-cross wafers, we also identify the exposure relationships required to achieve circular patterns.

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