

Tuesday Evening Poster Sessions, November 14, 2006

Nano-Manufacturing Topical Conference Room 3rd Floor Lobby - Session NM-TuP

Nano-Manufacturing Poster Session

NM-TuP1 Glass Nanoimprint using Amorphous Ni-P Mold Etched by Focused Ion Beam, H. Mekarū, National Institute of Advanced Industrial Science and Technology (AIST), Japan; **T. Kitadani,** SAWA PLATING CO.,LTD., Japan; **M. Yamashita,** Hyogo Prefectural Institute of Technology, Japan; **M. Takahashi,** National Institute of Advanced Industrial Science and Technology (AIST), Japan

We succeeded in the glass nanoimprint of line and space patterns using an amorphous Ni-P mold. The glass-like carbon has been used as a mold material to mold not only Pyrex glasses but also quartz glasses because it's still stable in the temperature of 1650 °C. However, it is difficult to process a quartz glass substrate to arbitrary shape by machining. We thought that the amorphous Ni-P alloy is used as a mold material for the industrial glass molding. To replicate on Pyrex glasses, the mold material should endure the heating of 600 °C or more. Pyrex glasses should be able to release from the mold without a release agent. We thought that there is a possibility that the wettability between Ni and Pyrex glasses decreases if the crystal Ni layer is changed into an amorphous layer like a glass-like carbon. If Ni is electroless plated mixing suitable amount of P on a Si wafer or a Ni substrate, the Ni-P layer becomes amorphous. The ratio of appropriate Ni and P was judged from the X-ray diffraction measurement, and the optimized composition ratio of Ni-P was Ni : P = 92 wt% : 8 wt%. After electroless plated, the amorphous Ni-P layer was heat-treated at 400 °C to improve the hardness. Moreover, line and space patterns of line width less than 1 μm was etched with FIB on the mold, and the processing accuracy of the amorphous Ni-P layer was compared with the pure Ni layer. As a result, patterns of several 100 nm width can be fabricated to depth 1 μm on the amorphous Ni-P mold, and processed side walls were smooth. At pure Ni layer, the processing line was notched, and the side walls were very rough. The crystal size of the pure Ni layer was measured by the TEM observation, and the maximum crystal size was 500 nm. The crystal grain seems to hinder in the processing of the nano-pattern. Line and space patterns of the amorphous Ni-P mold was nanoimprinted on a Pyrex glass using the glass embossing device (ASHE0201) that AIST had developed.

NM-TuP2 Annealing Effect of Structural, Morphological and Optical Properties on Reactive Sputtered WO₃ Films for Mediated Heterogeneous Photocatalyst, K. Prabakar, T. Takahashi, K. Takahashi, T. Nezuka, University of Toyama, Japan; **T. Nakashima,** Kashiwa Chuo High School, Japan; **Y. Kubota,** University of Yokohama City, Japan; **A. Fujishima,** Kanagawa Academy of Science and Technology, Japan

The WO₃ mediated heterogeneous photocatalyst for the oxidation of pollutants in air would be useful study for environmental decontamination purposes. Reactive facing target sputtering method was used to deposit WO₃ thin films from a metal tungsten disc in an Ar+O₂ mixture gas atmosphere at different sputtering pressures. X-Ray diffraction, scanning electron microscopy, UV-vis spectrophotometer in the wavelength range 300 to 900 nm and Raman spectroscopy studies were performed to study structural, surface morphology and the optical properties of the as-deposited and annealed samples. Annealing treatments were done in oxygen atmospheres. All the as-deposited films were amorphous in structure. The films annealed at 400°C and deposited at 100 W have monoclinic crystal structure with the preferential orientation of (111) plane. As the sputtering power increases to 200 W and annealed at 400°C, a changes in the crystalline orientation of the films along the (001) direction is observed. SEM images show a denser granular structure with grains having different shapes and sizes. The WO₃ films deposited at the sputtering pressure of 0.15 Pa and annealed at 400°C show the nanorods like growth from the observation of SEM images. The optical absorption edge of the as-deposited films prepared at the sputtering pressures of 0.8 - 0.15 Pa varied between 340 - 380 nm and shifted up to 470 nm when the samples are annealed at 400 °C. From the measurement of Raman spectra, it was observed that the O - W⁶⁺ - O bonds, and the W⁶⁺=O stretching mode of terminal atoms on the surface of WO₃ microcrystalline grains. The suitability of the films for the WO₃/TiO₂ heterogeneous photocatalyst were analyzed and discussed.

NM-TuP3 High-K HfO₂ Nanotube Fabrication using Template Synthesis and Atomic Layer Deposition, I. Perez, E. Robertson, L. Henn-Lecordier, H. Yi, S.J. Son, S.B. Lee, University of Maryland, College Park; **G.W. Rubloff,** University of Maryland, College Park, US

In a template synthesis approach, we have exploited self-assembly which occurs during the anodic oxidation of aluminum to produce anodic aluminum oxide (AAO) membranes with high densities of cylindrical nanopores with uniform dimensions and spacing. The high aspect ratio of the pores (up to 1000:1), their nanoscale dimensions (diameters 15-100 nm), and their large area density (~10¹¹ pores per cm²) suggest diverse applications, from nanowire and nanotube structure fabrication to gas and chemical separations, electronic nanocomponents, and nano-energy products. To achieve more precise control of nanostructure fabrication on AAO membrane templates, we have applied atomic layer deposition (ALD) to produce high-K HfO₂ nanotubes in AAO templates, which serve as scaffolds for nanofabrication of nanotubes. We then release the HfO₂ nanotubes by dissolution of the alumina template. TEM shows the HfO₂ nanotubes to have wall thicknesses 3-5 nm and lengths 2.5-3.5 μm. ALD employs alternating reactant exposures and essentially self-limiting adsorption/reaction of organometallic precursors and oxidants to achieve atomic-scale control of deposited films. With self-assembly and self-limiting reaction dominating the template and nanotube fabrication steps, this combination appears attractive to meet the future demands of nanotube manufacturing. @footnote 1@ @FootnoteText@ @footnote 1@Sponsored in part by the Laboratory for Physical Sciences.

NM-TuP4 Fabrication of Titanium Oxide Nanotubes by Anodization, K. Ishibashi, H. Sato, R. Yamaguchi, Y. Kimura, M. Niwano, Tohoku University, Japan

Dye-sensitized solar cells (DSSCs) have been an attractive device with their simple structure and cost effectiveness. DSSCs were generally constructed with a TiO₂ electrode, electrolyte containing iodine and a Pt counter electrode. It is important to adsorb a lot of dyes on the TiO₂ electrode for fabricating high-effective DSSCs and the TiO₂ electrode with large surface area is required. Using the TiO₂ electrode with porous structures is a solution to it. On the other hand, several groups have reported that diffusion coefficients of electron in mesoporous TiO₂ are much lower than those in the bulk crystal because of electron scattering due to grain boundaries between TiO₂ nanoparticles, oxygen defects, and amorphous layers. Therefore, TiO₂ nanotubes or nanowires are a promising class of materials to improve energy conversion efficiency of DSSCs because they have a large surface area comparable to mesoporous TiO₂ and few grain boundaries. In fact, it was reported that the use of TiO₂ nanowires improves the energy conversion efficiency. However, production of those TiO₂ nanotubes requires high temperature and a reaction time of several dozens hours. In this study, we demonstrate that TiO₂ nanotubes can be synthesized at room temperature for several minutes using an electrochemical process. We prepared a sheet of 99.5% Ti and anodized it at a potential of 40 V in a mixture of perchloric acid and ethanol using Pt as a counter electrode. The length and the diameter of the TiO₂ nanotubes we obtained were more than 10 μm and about 70 nm, respectively.

NM-TuP5 Fabrication of Nanometer-scale Holes Based on a Plasma Ashing and Selective Liquid Phase Deposition, K.S Kim, Y. Roh, Sungkyunkwan University, Republic of Korea

The fabrication of nanometer-scale structures such as nano-dot, nanowires, nano-pillars, nano-holes, etc. on single crystal semiconductor surface has recently attracted growing attention in the field of semiconductor device technologies. Such nano-fabrication is important not only for further advancement of conventional ULSI technologies but also for development of new-type devices such as quantum-effect ones. Particularly, nano-hole fabrication has been demonstrated by using advanced techniques such as nano-lithography using STM, atomic hydrogen etching and aluminum etching mask. However, these techniques have time consumption problem and require high production cost. Moreover, conventional deposition processes such as E-beam evaporation and sputtering have a thermal stress problem because of high process temperature. In this work, we have used plasma down stream ashing technique and selective liquid phase deposition. Using plasma down stream ashing and selective liquid phase deposition, we could fabricate the nanometer-scale pillar structures and nano-hole, respectively. Selective liquid phase deposition method is possible to deposit silicon dioxide under 50°C without damaging

Tuesday Evening Poster Sessions, November 14, 2006

the photoresist. We demonstrated less than 100 nm nano-holes and successfully reproduced in our experiment. These results may open the possibilities to fabricate the unique tools for the nanometer-scale diode, MOSFET, vertical-type field effect transistors and highly aligned emitters.

NM-TuP6 Fabrication of Binary Nano/Micro Sized Domain Composed of Alkyl and Fluoroalkylsilane Self-Assembled Monolayer, S.H. Lee, T. Ishizaki, N. Saito, O. Takai, Nagoya University, Japan

Self-assembled monolayers (SAMs) have attracted attention from a viewpoint of the functional surface modification such as physical, chemical and biological surface. In order to apply these SAMs to the practical application, it is vital to use lithography processes. Recently, several advances have been made in lithography methods for modifying functional groups on monolayer surfaces. Also, we have successfully fabricated functional surface with two different types of functional groups by modifying locally on an organosilane SAM by using vacuum ultraviolet (VUV) irradiation and scanning probe chemical conversion. However, the method was useful for specific surface functional group, the versatility was extremely low. In order to overcome the issue, it is required to establish more simple method. Here, we report a simple method to fabricate binary nano/micro sized domain composed of alkyl and fluoroalkylsilane SAM without lithography process. An octadecyltrichlorosilanes (OTS) and heptadecafluoro-1,1,1,2,2-tetra-hydrodecyltrichlorosilane (FOETS) were used as precursor molecules. Toluene (anhydrous, 99.8%) were used as the solvent. First, OTS-SAM domains structures were prepared on the silicon (111) substrates through a liquid phase method. In order to control the sizes of OTS-SAM domain structures, the deposition conditions were changed. The humidity and temperature conditions were changed from 5% to 50% and 5°C to 40 °C, respectively. After OTS-SAM preparation, the FOETS-SAM was prepared on the silicon oxide uncovered with OTS-SAM. The humidity and temperature conditions for FOETS-SAM were 50% and 20°, respectively. We found that the preparation conditions allowed us to control of the OTS-SAM domain size. And we confirmed that nano/micro sized domain composed of alkyl and fluoroalkylsilane SAM was formed on the silicon oxide substrate by using atomic force microscope (AFM) and Kelvin probe force microscope (KPFM).

NM-TuP7 Molecular-Beam Epitaxy of InN Quantum Dots on Nitrided Sapphire, Y.E. Romanyuk, University of California at Berkeley and Lawrence Berkeley National Laboratory, US; R.-G. Dengel, S.R. Leone, University of California at Berkeley and Lawrence Berkeley National Laboratory

Recent investigations suggest that the bandgap of InN is approximately 0.7 eV, rather than the previously accepted value of 1.8-2.0 eV, making InN a highly desirable component for potential band-gap-tunable optical applications. In this work, InN quantum dots (QDs) are grown by rf-plasma-assisted molecular beam epitaxy on thin nitride layers produced directly on sapphire substrates. Previous studies obtained InN QD growth on substrates or thick buffer layers of Si, GaN, and AlN. The nanostructures in this work are produced directly on nitrided c-cut sapphire substrates. The nitridation of sapphire for a period of one hour at 950°C results in the formation of a rough AlN surface layer, which acts as a very thin buffer and facilitates the nucleation of the InN QDs. A series of InN QD samples are grown at various substrate temperatures from 420°C to 500°C under slightly nitrogen-rich conditions. Ex situ AFM images reveal that the average InN growth rate is limited by the In flux on the surface, and the QD morphology depends strongly on the substrate temperature. Well-confined InN nanoislands with the greatest height / width ratio of 0.2 can be grown at 460°C. Lower substrate temperatures result in a reduced aspect ratio due to lower diffusion rate of the In adatoms, whereas the thermal decomposition of InN complicates the growth at T>500°C. The densities of separated QDs vary between $1.5 \times 10^{10} \text{ cm}^{-2}$ and $3.0 \times 10^{10} \text{ cm}^{-2}$ depending on the growth time. Typical island heights are 3-10 nm, and therefore, carrier confinement is expected in vertical direction in a part of the fabricated dots. For the investigation of optical properties, work is in progress to encapsulate the QDs to avoid the formation of surface states that suppress radiative recombination. The demonstration of the intrinsic photoluminescence of InN QDs would give a possibility to use InN nanostructures in photonic devices.

NM-TuP8 AFM Tip-Characterize Fabricated from Compound Semiconductor Superlattices, H. Itoh, T. Fujimoto, S. Ichimura, RIIF-AIST, Japan

A tip characterizer for atomic force microscope (AFM) was developed to analyze the accurate tip-shape and limitation of the resolution of each tip on the cantilever. Recently, many kinds of sharp tips are supplied from

many vendors, and tip radius of the conventional AFM tip is typically 10nm. It is necessary to fabricate nano-structures, which are smaller than tip radius, to carry out in situ analysis of the probe apex. Additionally, the nano-structures as a tip-characterizer must be fabricated accurately and variation of the shapes should be lower than tip radius by several times to prove accuracy of measured shape of AFM probe. A cross section of superlattices, which was made from compound semiconductor, was used to achieve accurate shape of the nano-structures. Superlattices of InGaP and GaAs were grown on the GaAs substrate. InGaP layers were controlled to be accurate thickness, which was the width of the line to characterize the tip. GaAs area was etched selectively from the cross section of the wafer. It is possible to fabricate fine lines which are thinner than 10nm. Line widths were measured by transmission electron microscopy and accuracy was measured from lattice images. Error of the twenty-nanometer-lines was less than 10% of the width and radius of the edge was lower than 3nm. Cross section of probe-tip can be measured easily from the line profile of AFM image, and it is easy to estimate deterioration of tip-shape after taking images. It is possible to estimate the deterioration of commercial tip radius in the range of 5 to 30nm, and shape of the cross section of probe-tip can be measured in the accuracy of 3nm in the range of apex radius from 10 to 30nm. This work was partially supported by Japan Science and Technology Agency.

Author Index

Bold page numbers indicate presenter

— D —

Dengel, R.-G.: NM-TuP7, **2**

— F —

Fujimoto, T.: NM-TuP8, **2**

Fujishima, A.: NM-TuP2, **1**

— H —

Henn-Lecordier, L.: NM-TuP3, **1**

— I —

Ichimura, S.: NM-TuP8, **2**

Ishibashi, K.: NM-TuP4, **1**

Ishizaki, T.: NM-TuP6, **2**

Itoh, H.: NM-TuP8, **2**

— K —

Kim, K.S.: NM-TuP5, **1**

Kimura, Y.: NM-TuP4, **1**

Kitadani, T.: NM-TuP1, **1**

Kubota, Y.: NM-TuP2, **1**

— L —

Lee, S.B.: NM-TuP3, **1**

Lee, S.H.: NM-TuP6, **2**

Leone, S.R.: NM-TuP7, **2**

— M —

Mekaru, H.: NM-TuP1, **1**

— N —

Nakashima, T.: NM-TuP2, **1**

Nezuka, T.: NM-TuP2, **1**

Niwano, M.: NM-TuP4, **1**

— P —

Perez, I.: NM-TuP3, **1**

Prabakar, K.: NM-TuP2, **1**

— R —

Robertson, E.: NM-TuP3, **1**

Roh, Y.: NM-TuP5, **1**

Romanyuk, Y.E.: NM-TuP7, **2**

Rubloff, G.W.: NM-TuP3, **1**

— S —

Saito, N.: NM-TuP6, **2**

Sato, H.: NM-TuP4, **1**

Son, S.J.: NM-TuP3, **1**

— T —

Takahashi, K.: NM-TuP2, **1**

Takahashi, M.: NM-TuP1, **1**

Takahashi, T.: NM-TuP2, **1**

Takai, O.: NM-TuP6, **2**

— Y —

Yamaguchi, R.: NM-TuP4, **1**

Yamashita, M.: NM-TuP1, **1**

Yi, H.: NM-TuP3, **1**