

Thin Film Division

Room: East Exhibit Hall - Session TF-TuP

Thin Films Poster Session

TF-TuP1 Spatially Varied Orientation Selective Epitaxial Growth of CeO₂(100) and (110) Areas on Si(100) Substrates by Reactive Magnetron Sputtering Utilizing Electron Beam Irradiation. *T. Inoue, S. Shida*, Iwaki Meisei University, Japan

Cerium dioxide is of great interest due to favorable properties as an electronic material, such as high dielectric constant of 26, high chemical stability, transmission in visible and infrared regions, and high efficient ultra-violet absorption. Epitaxial growth of CeO₂ layers on Si substrates has been studied making the best use of a close lattice parameter matching relation. Recently, we have found that orientation selective epitaxial (OSE) growth of (100) and (110) oriented CeO₂ layers on Si(100) is capable by controlling surface potential distribution in reactive magnetron sputtering. Non-polar CeO₂(110) grows on Si(100) with usual non-modified surface potential, whereas polar CeO₂(100) grows on Si(100) with adequately bent surface potential. We are studying two OSE control methods, one is substrate bias application[1] and the other is low energy electron beam irradiation.[2,3] The latter has the attractive possibility of spatially varied two dimensional control of OSE grown regions.[4] This paper describes experimental results of electron beam induced OSE growth with patterned scanning of 90 eV electron beams. The size and position of the electron beam irradiation area were controlled using absorbed electron current image observation. RHEED and XRD analyses proved the realization of two dimensionally controlled OSE growth of CeO₂(100) and (110) areas in electron beam irradiated and non-irradiated areas, respectively. Precise XRD peak profile measurements revealed that there are considerably wide transition regions in between the above two areas, which contain both orientation components. For the application to two dimensionally patterned hybrid orientation technology, the transition region width should be reduced significantly. Our experiments clarified that the width of the transition region reduces proportionally with the logarithm of underlying Si substrate resistivity, reflecting the surface spread of potential distribution. These results will lead to sophisticated microelectronics devices using hybrid orientation technology. This work was supported by KAKENHI (20560024). A part of this work were conducted at the AIST Nano-Processing Facility, supported by "Nanotechnology Network Japan" of the MEXT, Japan.

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TF-TuP2 Influence of Growth-Rate on the Epitaxial Orientation and the Crystalline Quality of CeO₂ Thin Films Grown on Al₂O₃(0001) by Molecular Beam Epitaxy. *M.I. Nandasiri*, Western Michigan University, *P. Nachimuthu, T. Varga, V. Shutthanandan, W. Jiang, S.V.N.T. Kuchibhatla, S. Thevuthasan*, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida, *A. Kayani*, Western Michigan University

Cerium oxide (CeO₂) is one of the extensively studied rare earth oxides; however, it continues to attract attention because of its potential use in medical biology, catalysis, intermediate temperature solid oxide fuel cells (IT-SOFC), and resistive oxygen gas sensors. Driven by the need for fundamental understanding of its unique properties, CeO₂ thin films grown on various substrates by different methods at different experimental conditions have been extensively studied. However, the influence of growth-rate on the orientation and the crystalline quality of the CeO₂ thin films is relatively unexplored. While understanding the influence of growth-rate, we evaluated the ability to tailor the orientation and the epitaxial quality of CeO₂ films on Al₂O₃(0001).

CeO₂ thin films were grown on Al₂O₃ (0001) substrates at 650°C with different growth-rates (1-10 Å/min) by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The growth rate induced epitaxial orientations and crystalline quality of CeO₂ thin films were studied by in-situ reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and x-ray diffraction (XRD) techniques. CeO₂ grows as three-dimensional (3-D) islands and two-dimensional (2-D) layers at growth-rates

of 1-7 Å/min and ≥9 Å/min, respectively. AFM images show average surface roughness of 5-10 Å, indicating the high-quality surfaces of CeO₂ thin films. The formation of epitaxial CeO₂(100) and CeO₂(111) thin films occurs at growth rates of 1 Å/min and ≥9 Å/min, respectively. Glancing incidence XRD measurements have indicated that the films grown at intermediate growth rates (2-7 Å/min) consist of some polycrystalline CeO₂ along with CeO₂(100). As indicated by x-ray pole figure measurements, the CeO₂ thin film grown at 1 Å/min shows six in-plane domains, characteristic of well-aligned CeO₂(100) crystallites. When increasing the growth rate from 1 Å/min to 2-7 Å/min, poorly-aligned CeO₂(100) crystallites start to coexist along with well-aligned crystallites. The content of the poorly-aligned CeO₂(100) crystallites increases with increasing growth rate from 2 Å/min to 7 Å/min, and three out of six in-plane domains gradually decrease and eventually disappear. At growth rates ≥9 Å/min, CeO₂(111) film with single in-plane domain was identified. The formation of CeO₂(100) 3D-islands at growth rates of 1-7 Å/min is a kinetically-driven process unlike at growth rates ≥9 Å/min, which result in an energetically and thermodynamically more stable CeO₂(111) surface.

TF-TuP3 Influence of Target Type on Surface Texture-etched AZO Films Prepared by Magnetron Sputtering for Solar Cell Transparent Electrode Applications. *T. Minami, T. Miyata, T. Hirano, Y. Noguchi, J. Nomoto*, Kanazawa Institute of Technology, Japan

This paper describes the influence of sintered oxide targets on the surface texture formation as well as light management obtainable by wet-chemically etching transparent conducting Al-doped ZnO (AZO) thin films prepared by different types of magnetron sputtering depositions (MSD). For transparent electrode applications in thin-film solar cells based on CuIn_{1-x}Ga_xSe₂ and Si, transparent conducting AZO thin films require an appropriate surface texture to improve photovoltaic properties through induced light scattering and subsequent light trapping. It was found that the suitability of the light scattering characteristics for thin-film solar cell applications was considerably dependent on both the type of AZO target and the type of MS deposition used.

The surface texture-etched AZO thin films were prepared by a d.c.- or r.f. (13.56 MHz) power-superimposed d.c.- magnetron sputtering deposition (dc-MSD or rf+dc- MSD) with sintered AZO targets that was followed by a heat treatment with rapid thermal annealing (RTA) and a subsequent wet-chemical etch. Five types of commercially available high-density-sintered rectangular AZO targets were used. The suitability of the light scattering characteristics for thin-film solar cell applications was evaluated by carrying out surface texturing of the samples with wet-chemical etching in a 0.1% HCl solution conducted after the heat treatment with RTA (at a temperature of 300-500°C for 1-5 min in air). It was found that the obtainable surface texture as well as the haze value in the range from visible to near infrared were considerably affected by not only the AZO target used but also the type of MSD; the dc- and rf+dc-MSD were conducted using the five types of targets with properties that depended on the supplier. The surface-textured AZO thin films prepared by rf+dc-MSD and etched to an appropriate depth after RTA were found to exhibit a higher haze value and a lower resistivity than the values exhibited by equivalent films prepared by dc-MSD. It was also found from X-ray diffraction analyses that the as-deposited AZO thin films prepared by rf+dc-MSD exhibited better crystallinity than those prepared by dc-MSD; also, the crystallinity of AZO thin films, such as the c-axis orientation, was slightly improved by the RTA treatment. A high haze value generally above 70% in the range from visible to near infrared (at wavelengths up to 1200 nm), which is suitable for thin-film solar cell applications, was obtained in the best surface-textured AZO thin films: film thickness of 2 μm prepared by rf+dc-MSD with an appropriate AZO target and etched to a depth of approximately 300 nm after RTA at approximately 500°C for 5 min.

TF-TuP4 XPS and ToFSIMS Characterization of Laser Modified Films for Li-Ion Battery Cathodes. *M. Bruns, R. Kohler, J. Proell, C. Ziebert, W. Pflöging*, Karlsruhe Institute of Technology, Germany

The development of novel electrode materials for lithium-ion batteries has become subject of great interest in recent years due to the necessity of improved performance for future mobile applications and energy storage systems. Therefore, a great deal of effort has been spent to develop strategies for the enhancement of battery lifetime, capacity, and cyclability. A self-evident goal to improve the electrochemical properties of cathode materials is to enhance the lithium intercalation rate by increasing the surface to bulk ratio. For this purpose, a very promising approach is the laser-assisted surface modification and structuring of commonly as a cathode material used lithium cobalt oxide and lithium manganese oxide.

The present study focuses on the characterization of non-structured and laser modified films before and after electrochemical cycling using a

combination of complementary surface analytical methods. For this purpose rf magnetron sputtered lithium cobalt oxide and lithium manganese oxide were structured with laser radiation leading to a surface microstructure with increased active surface area. In particular, high repetition excimer laser radiation with a pulse width of 4-6 nm and 248 nm wavelength was used. Self-organized conical microstructures were formed using laser fluences between 0.5 J/cm² and 2.0 J/cm². A subsequent annealing process using high power diode laser radiation at 940 nm wavelength enables the adjustment of the required crystallinity.

X-ray photoelectron spectroscopy (XPS) provides the chemical composition in a non-destructive manner. The in-depth distribution of the electrode constituents and the solid electrolyte interface after cycling was studied by time-of-flight secondary mass spectrometry (ToFSIMS) and XPS sputter depth profiles. In addition, the conical topography was shown by scanning electron microscopy (SEM) and crystallinity was proven by X-ray diffraction.

TF-TuP5 Effect of Temperature on the Native Oxide Consumption during the ALD of Ta₂O₅ and TiO₂ on GaAs (100) Surfaces, L. Ye, T. Gougousi, UMBC

Thermal ALD processes for the deposition of TiO₂ and Ta₂O₅ have been developed using amide precursors and H₂O as reagents. The TiO₂ films were deposited from tetrakis dimethyl amido titanium and H₂O and the Ta₂O₅ films were deposited from pentakis dimethyl amido tantalum and H₂O. The growth rate for both processes was ~0.6 Å/cycle at 200°C and 250°C respectively. These temperatures represent the so-called ALD minimum. At these temperatures the existence of a reaction that leads to the consumption of the surface native oxides during depositions on GaAs (100) surfaces has been confirmed using x-ray photoelectron spectroscopy and high resolution transmission electron microscopy. To investigate the effect of temperature on the native oxide consumption rate two sets of samples with thickness 2 and 3 nm have been prepared at temperatures ranging from 100 to 350°C. For both ALD chemistries a significant enhancement in the gallium and arsenic oxide consumption rate was observed for process temperatures above 300°C. For depositions performed at temperatures more than 50°C below the ALD minimum the consumption reaction is significantly slower.

TF-TuP7 Influence of Doped Al Content on Electrical Properties and Light Management Obtainable by Texture-etched AZO Films Prepared by DC Magnetron Sputtering, J. Nomoto, T. Miyata, T. Hirano, T. Minami, Kanazawa Institute of Technology, Japan

Al-doped ZnO (AZO) thin films that would be suitable for transparent electrode applications in thin-film Si-based solar cells must necessarily attain not only a decrease of plasma resonance frequency by lowering the carrier concentration while retaining a resistivity on the order of 10⁻⁴ Ωcm, but also a significant scattering of light incident on the film by surface texturing. In this paper, we describe the influence of doped Al impurity content on the electrical properties as well as the light management obtainable by surface texture-etched AZO thin films that were prepared with various Al contents by a dc magnetron sputtering (dc-MS) deposition and wet-chemically etched after a rapid thermal annealing (RTA) treatment. In addition, the stability of the resulting electrical properties for practical use in various environments was investigated for these AZO films prepared with various Al contents.

Transparent conducting AZO thin films were prepared with a thickness up to 2μm by a dc-MS deposition using sintered AZO targets that had various Al contents. The basic sputter depositions were carried out on OA-10 glass substrates at a temperature of 200°C in a pure Ar gas atmosphere at a pressure of 0.4Pa and a power of 200W. Surface texturing of the AZO thin films was carried out by wet-chemical etching in a 0.1mol/l HCl solution after the thin films were heat treated with RTA at a temperature of 300-500°C for 1-5min in air. It was found that the obtainable surface texture and electrical properties in texture-etched AZO thin films were considerably affected by the RTA treatment conditions as well as the Al content doped into the films. The transmittance in the near-infrared region of the resulting AZO thin films exhibited a tendency to improve as the RTA temperature was increased. A high transmittance above 80% at a wavelength of 1.2μm was obtained in 1-μm-thick-AZO thin films prepared under the following conditions: an Al content (Al/(Al+Zn) atomic ratio) of approximately 0.5at.% when the thin films were heat treated without RTA and an Al content below 1.5at.% when the thin films were heat treated with RTA. In addition, when the thin films were heat treated with RTA at 500°C for 3-5min, increasing the Al content doped into the AZO films enhanced the transmittance in the near infrared region, irrespective of the film thickness. However, it should be noted that the optimal Al content doped into texture-etched AZO thin films that would be suitable for transparent electrode applications in thin-film Si-based solar cells was considerably dependent on the obtainable crystallinity in the films as well as whether the thin films were heat treated with RTA or not.

TF-TuP9 Structure and Photo-Functional Properties of N⁺ Ion Irradiated TiO₂ Thin Film under Various Substrate Temperatures, H. Shukur, M. Sato, Kogakuin University, Japan, I. Nakamura, Tokyo Metropolitan Industrial Technology Research Institute, Japan, I. Takano, Kogakuin University, Japan

Titanium dioxide (TiO₂) has been fundamentally used as a photocatalytic application to decompose environmental pollution materials. TiO₂ can generate active oxygen by exposing to sunlight and also is harmless to the environment and the low cost material, so that it is expected to use as an element of a clean energy system in the future.

TiO₂ shows relatively high reactivity and chemical stability under UV light whose energy exceeds the band gap of 3.2 eV for the anatase crystalline phase and 3.0 for the rutile crystalline phase. Many techniques has been examined to increase its activity under visible light region.

N⁺ ion irradiation method has been used by many researchers because it can provide an activated TiO₂ in both of visible and UV light. However the collision between ion and film causes a defect in film structure as causing a decline in photo-functional property.

In this study structural, chemical and photo-functional properties of TiO₂ thin film with a rutile structure were studied after irradiation by various doses of N⁺ ion beam under various temperatures. Reactive magnetron sputtering method was employed to prepare TiO₂ thin film on glass substrate (corning #1737). Ti-O was sputtered from Ti target in an Ar / O₂ gas and the substrate was heated at 300 °C. The total film thickness was around 180 nm with a deposition rate of 0.025nm/sec. N⁺ ion was irradiated to TiO₂ thin film under 15 keV in acceleration voltage, and 40 μA/cm² in ion current density with a various implantation doses. Substrate temperature was set at a room temperature (25 °C), 100, 200 and 300 °C through ion irradiation processes. The structure was determined by X-ray diffraction (XRD: MAC Science High quality XG M18XCE) with CuKα (0.154nm) radiation at an incident angle of 0.3°, and the composition was characterized by X-ray photoelectron spectroscopy. The photocatalyst property was measured by a MB immersion test. The spectrophotometer (SHIMADZU UV-2550) was used to measure the difference in light absorption at a wave length of 665nm.

The increasing in the Full Wave Half Maximum (FWHM) of XRD measurements with N⁺ ion irradiation under 25°C refers to declining of the crystal structure of the TiO₂ thin film. On the other hand HMFV decreased by increasing the substrate temperature and closed to the value of the as-deposited film prepared under 300 °C. Thus the improvement of photocatalytic property under visible light was increased from 9.1% at 25 °C to 25.7% at 300 °C under the same N⁺ irradiation (2.5x10¹⁵ions/cm²).

TF-TuP11 Study of Electronic Structure in In-Ga-ZnO Amorphous Semiconductor Films, Y. Li, Z. Liu, X. Hu, J. Ren, Xi'an Jiaotong University, China

Amorphous oxide semiconductor In-Ga-ZnO (IGZO) has unique electron transport properties such as large electron mobility (10-30 cm²/Vs) and good uniformity for active-matrix flat panel display applications [1-2]. Theoretical studies indicate the high electron mobility in amorphous IGZO is due to spherically spread orbitals of metal cations forming unaffected electron transport path. It has been proposed amorphous IGZO has strong ionic electronic structure compared to the covalent electronic structure in amorphous Si [3]. However, the transport mechanism to result in high electron mobility in amorphous structure has not been experimentally explained yet. The focus of this study is to use surface probe, optical as well as Raman spectroscopic techniques to investigate the electronic structure in IGZO. Amorphous IGZO thin films are being grown at room temperature by pulsed laser deposition. Initial Hall effect measurements indicate that amorphous IGZO films have electron concentration of 9×10¹⁹ cm⁻³ with Hall mobility of 16.8 cm²/Vs. Raman spectroscopy is being used to analyze the lattice arrangement, i.e. the amorphous state and the bonding properties in IGZO films. During film processing, hydrogen is being introduced into the material system to modulate the defect state levels and band gap structure in IGZO. X-ray photoelectron spectroscopy is being used to obtain the valence band spectrum of IGZO films. The energy state within the band gap is being analyzed using deep level transient spectroscopy. The correlation of growth parameters on optical properties as well as electronic structure will be described in this work.

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