

Thursday Afternoon Poster Sessions

Electronic Materials and Processing

Room: Hall D - Session EM-ThP

Electronic Materials and Processing Poster Session

EM-ThP1 Effect of Water Immersion and Surface Compositional Profile of Photoacid Generator Molecules in Photoresist Materials, S. Sambasivan, Suffolk Community College, V.M. Prabhu, D.A. Fischer, National Institute of Standards and Technology, L.K. Sundberg, R.D. Allen, IBM Almaden Research Center

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling in the top 2 to 6 nm range of photoacid generators (PAG) in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. A comparative study of the surface composition of PAG (TPS-PFOS, TPS-PFBS and TPS-Triflate) in photoresist system before and water immersion was monitored via NEXAFS. Results reveal that the loss of PAG occurs after the water immersion in all the three different PAG system examined. Detailed quantification of the PAG loss due to water immersion was seen to critically depend on the size of the PAG and its solubility in water. TPS-PFOS photoacid generator largest in size despite its least solubility in water showed the maximum loss after water immersion followed by TPS-PFBS and TPS-Triflate. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

EM-ThP2 Direct Evidence for Post-Crystallization Germanium Precipitation in Thin Films of Phase-Change Material $\text{Ge}_{15}\text{Sb}_{85}$, C. Cabral, Jr., L. Krusin-Elbaum, IBM T.J. Watson Research Center, S. Raoux, V.R. Deline, IBM Almaden Research Center, J. Bruley, A. Madan, T.L. Pinto, IBM Hudson Valley Research Park

We present evidence for the instability in the crystalline metallic phase of eutectic phase-change $\text{Ge}_{15}\text{Sb}_{85}$ thin films considered for integration into nonvolatile embedded memory cells. Te-free phase-change materials, owing to a combination of higher crystallization temperatures and the absence of easily diffusing chalcogen atoms, offer an advantage over the ternary chalcogenides, provided that the material is stable throughout the switching process. We find that while the amorphous (semiconducting) phase is robust until $\text{Ge}_{15}\text{Sb}_{85}$ film's crystallization into a rhombohedral structure at 240°C, at 350°C, Ge rapidly precipitates out, aggregating at the film's grain boundaries and interfaces. Ge precipitation, visualized directly with transmission electron microscopy and in-situ x-ray diffraction, is found to be exothermic by differential scanning calorimetry, and is found to affect films' reflectivity, resistance, and stress. Such changes could impact switching reliability, with additional doping required to minimize the precipitation process.

EM-ThP3 Development of a Polycrystalline Zinc Oxide Scintillator for Radiation Detection, D.M. DeVito, J.S. Neal, B.L. Armstrong, Oak Ridge National Laboratory, M. Hong, University of California - Davis, B. Kesanli, J.O. Ramey, J.Y. Howe, Oak Ridge National Laboratory, X. Yang, N.C. Giles, West Virginia University, Z.A. Mumir, University of California - Davis, L.A. Boatner, Oak Ridge National Laboratory

N-type doped ZnO is an ideal scintillator for use as an alpha particle detector due to its high light output, chemical stability, and sub-nanosecond decay times. ZnO, being a non-cubic material, has seen little success in producing the highly transparent polycrystalline bodies needed for scintillator applications. In this work, ZnO:Ga and ZnO powders were pressed into high density (>98%) polycrystalline bodies by hot uniaxial pressing and spark plasma sintering. These samples showed both photoluminescence and emission under alpha particle exposure. Investigation of the sample microstructure showed substantial grain growth. Samples also showed a high degree of translucency after post-sintering heat treatments. Additional processing results will also be included.

EM-ThP4 Structure and Optical Behavior of Sputter Deposited Hafnia-Alumina Nanolaminate Films, E.E. Hoppe, M. AlMomani, C.R. Aita, University of Wisconsin-Milwaukee

Nanolaminate films of polycrystalline HfO_2 and amorphous Al_2O_3 were grown by reactive sputter deposition on unheated fused SiO_2 and the nascent oxide of <111> Si. Many different bilayer architectures were examined. The films were air annealed at 573 K to 1273 K, and analyzed by double angle x-ray diffraction and ultraviolet-visible spectrophotometry. X-ray diffraction showed the amount of monoclinic HfO_2 (the bulk equilibrium phase) decreased with decreasing HfO_2 layer thickness. Previous high resolution transmission electron microscopy results¹ showed that the initial HfO_2 phases present in ultrathin layers were tetragonal and orthorhombic, consistent with a finite crystal size effect. Annealing of the as-grown nonmonoclinic structure at temperature up to 973 K produced no gross structural change. Annealing at 1173 K produced a metastable mixed cation tetragonal phase, $\text{Hf}_{1-x}\text{Al}_x\text{O}_{2-z}$, that is isomorphous with tetragonal HfO_2 . This mixed cation phase became unstable at 1273 K and phase-separated into monoclinic HfO_2 and amorphous Al_2O_3 . In all cases, the fundamental optical absorption edge was found to consist of two distinct regions with respect to incident photon energy. Significant O 2p \rightarrow Hf 5d interband absorption occurred at energy $E \geq 6.2$ eV. For $E < 6.2$ eV, films with nonmonoclinic structure retained a (desirable) featureless optical absorption edge despite further (nano)crystallization, including the formation of $\text{Hf}_{1-x}\text{Al}_x\text{O}_{2-z}$. Films with a monoclinic structure developed a pre-gap absorption band found to be characteristic of the seven-fold Hf-O coordination in the single layer monoclinic HfO_2 .² We relate this undesirable pre-gap absorption band to self-trapped excitons that can form in the monoclinic structure.³

¹ E.E. Hoppe, M. Gajardziska-Josifovska, and C.R. Aita, Appl. Phys. Lett. 91, 203105 (2007).

² E.E. Hoppe, R.S. Sorbello, C.R. Aita, J. Appl. Phys. 101, 123534 (2007).

³ D. Muñoz Ramo et al. PRL 99, 155504 (2007).

EM-ThP5 Properties of Mn Doped ZnO Hollow Nanosphere Structures, D.-R. Liu, C.-C. Kei, C.-Y. Su, W.-C. Chen, National Applied Research Laboratories, Taiwan

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, Al_2O_3 layer was conformally deposited on the surface of polystyrene (PS) nanosphere by atomic layer deposition (ALD). After removal of PS nanosphere by heating, alumina hollow nanospheres were formed. Then the $(1-x)\text{Zn}(x)\text{MnO}$ hollow nanosphere were grown by Nd:YAG pulsed laser deposition (PLD). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were employed to characterize the surface properties of these samples. The high-resolution x-ray diffraction was used to evaluate the crystal quality. The magnetic properties of the $(1-x)\text{Zn}(x)\text{MnO}$ hollow nanosphere were measured by a superconducting quantum interference device (SQUID) magnetometer. Photoluminescence (PL) spectroscopy and spectrometer were used to characterize the optical properties. The results show that the properties of Mn doped ZnO hollow nanosphere strongly depend on the size of nanosphere.

EM-ThP6 Electrical Properties of Atomic Layer Deposited ZnO Thin Film Transistor with Various Channel Layer Thickness, W. Jeong, S. Bang, S. Lee, S. Jeon, S. Kwon, H.T. Jeon, Hanyang University, Korea

Wide band gap II-VI compound semiconductors have attracted much attention because of many potential applications for optoelectronic devices. Among these, ZnO thin films have been particularly interesting due to their potential applications in optoelectronic devices, such as light-emitting diodes, laser diodes, and transparent thin film transistor. Especially, ZnO-based thin film transistors (TFTs) have been intensively studied for flexible electronics, replacing conventional amorphous-Si TFT. Recently, there have been several reports on the fabrication of ZnO TFTs by means of rf magnetron sputtering, pulsed laser deposition, and chemical solution process. These methods need high process temperature or additional annealing process to obtain good transistor properties such as high mobility, low operation voltage. However, high temperature process is not suitable to apply for flexible substrates or organic dielectrics. Hence, we choose atomic layer deposition (ALD) method because ALD offers several advantages over the other techniques such as large area capability and good growth control in terms of homogeneity, composition, and thickness. Moreover, ALD process can be performed at low temperature. These merits are fundamental for a wide variety of applications requiring low thermal budgets. However, atomic layer deposited ZnO films exhibit high carrier

concentration ($n \sim 10^{18} \text{ cm}^{-3}$). The high channel carrier concentration in the oxide semiconductors is not suitable for TFT applications. Therefore, it is necessary to control the carrier concentration in order to build good quality ZnO-TFT. In this study, we varied thickness of ZnO in order to find optimal condition for thin film transistor. ZnO film on SiO₂/p-type Si substrate was deposited by ALD method using diethylzinc (DEZn) and H₂O at 110 °C and the thickness of ZnO film were varied from 40 nm to 70 nm as a function of ALD cycles. The crystallographic orientation of the ZnO films was determined by an X-ray diffractometer (XRD) with Cu K α radiation and the film morphology was analyzed by Atomic force microscopy (AFM) measurements. Device characterization was carried out at room temperature in the dark using an Agilent B1500A Semiconductor Analyzer. As a result, Ion/Ioff ratio was observed in 10^2 – 10^6 , saturation mobility was observed in $0.02 \sim 1.4 \text{ cm}^2/\text{Vsec}$.

EM-Thp7 Characterization of P-Si/SiO₂/N+Si Devices with Various Thickness of SiO₂, S.M. Lee, B.I. Son, K.H. Eum, I.S. Chung, Sungkyunkwan University, Korea

We attempted to evaluate n+Si/SiO₂/p-Si devices as a function of the thickness of SiO₂. The thickness of SiO₂ were varied from 2 nm to 5 nm. The breakdown of SiO₂ layer in n+Si/SiO₂/p-Si structure cause the device appears as pn+ junction diode. The simulated results using Silvaco TCAD also indicate that the currents of n+Si/SiO₂/p-Si structures increase exponentially with respect to the applied voltage in the forward bias region. In addition, as the SiO₂ breakdown is getting serious, the current-voltage curve moves toward the that obtained from ideal pn+ junction diode. The ratio in the current at 1.5 V between the breakdown device and the non-breakdown device reveals higher than 10000. The off state current in n+Si/SiO₂/p-Si structure was simulated based on the direct tunneling model. The fabricated devices reveals similar characteristics. However, as the thickness of SiO₂ layer decreases, the breakdown distribution and reliability tends to show worse results.

EM-Thp8 Role of Adsorbates in Surface Electron Accumulation on InN Films, R.P. Bhatta, A.R. Acharya, B.D. Thoms, M. Alevli, N. Dietz, Georgia State University

The presence of surface electron accumulation on a semiconductor has been shown to affect the properties of metallic contacts and may be important in determining other properties of devices. Adsorbates have been shown to affect the electron density on InAs surfaces, however, the effects on the surface electron concentration for InN have not been established. In this work, the effects of adsorbates on surface electron accumulation for N-polar InN have been studied by high resolution electron energy loss spectroscopy (HREELS). By varying the energy of the incident electrons the probing depth can be varied. Shifts in the energy of the conduction band plasmon indicate differences in plasma frequency and therefore differences in free carrier concentration as a function of depth from the surface. By this method it is shown that hydrogen-terminated N-polar InN exhibits surface electron accumulation. Heating InN for 15 minutes at 425°C desorbs the surface hydrogen without surface damage or film decomposition. HREELS of bare N-polar InN indicates the presence of surface electron accumulation and confirms that no surface indium is present. These results indicate that surface electron accumulation is not due to indium-indium bonding and is not affected by the presence or absence of surface hydrogen, but may instead be intrinsic to the N-polar InN surface. The effects of other adsorbates, such as oxygen, will also be discussed.

EM-Thp9 Effect of TCO Buffer Layer on the Growth of InN Film by MOMBE, W.-C. Chen, National Applied Research Laboratories, Taiwan, S.-Y. Kuo, Chang Gung University, Taiwan, H.-C. Pan, Gintech Energy Corporation, Taiwan, F.-I. Lai, Yuan Ze University, Taiwan, C.-N. Hsiao, National Applied Research Laboratories, Taiwan

In this paper, wurtzite structure Indium nitride films on TCO layer was examined. InN films were grown on highly-quality of TCO buffer layer by UHV-plasma assisted metal-organic molecule beam epitaxy system. We have studied influence of to growth temperature by their structure, surface morphology and optical properties. The InN films has been characterized in detail using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Transmittance electron microscopy(TEM),Hall effect. The surface roughness was obtained from SEM measurements with increased growth temperature. Furthermore, a pronounced two-dimensional growth mode was observed at the growth temperature of 500 °C, and InN films highly oriented to the c-axis were obtained by optimizing growth conditions in the direct growth on TCO buffer layer. TEM images show these InN films are single phase wurtzite crystals with preferred orientation along the c axis. Our results indicated that the growth temperatures of 500-550 °C were beat to achieve high quality InN films.

EM-Thp10 Synthesis of Ordered Arrays of (Ba_{0.6}Sr_{0.4})TiO₃ Nanotubes, G.H. Kim, K.T. Kim, C.I. Kim, Chungang University, Korea, Y.K. Yoon, University at Buffalo, the State University of New York

(Ba_xSr_{1-x})TiO₃ (BST) ferroelectrics exhibit high dielectric permittivity and have been widely investigated both in films and ceramics. Using BST ferroelectric structures, manufacturing highly integrated memory device is possible. Recently, one dimensional nanostructures, such as nanotube and nanofiber, have been intensively studied because of their unique structure and properties. However, the BST nanotube arrays have not been widely studied yet because of fabrication difficulty and its properties are not reported. The main aim of this work includes the fabrication and investigation of structural BST nanotube arrays prepared using the sol-gel method in an anodized nanoporous aluminum oxide template. The perovskite phase has been obtained as a function of the annealing temperature from 450 to 700 °C for 1h. The crystalline structures of the BST nanotubes arrays have been analyzed by X-ray diffraction. The surface and cross-sectional microstructures of BST nanotubes arrays are examined using scanning electron microscopy and transmission electron microscopy. The electrical P-E curve (hysteresis loop) of the BST nanotube array are illustrated.

EM-Thp11 Fabrication of Cerium Oxide Nanopillars for Oxygen Gas Sensor by Nanosphere Lithography, P.-J. Ko, J.-S. Park, H.-Y. Na, Chosun University, Korea, N.-H. Kim, Chonnam National University, Korea, W.-S. Lee, Chosun University, Korea

Cerium oxide (CeO₂) is one of the most widely used materials for the oxygen gas sensors. Sensing properties of CeO₂ is required to be improved by the fabrication to nanometer-scaled structure. The well-arrayed nanopillars of CeO₂ in a large area were fabricated by nanosphere lithography and oxygen plasma etching process. The spin coated CeO₂ thin films on silicon substrates by Sol-Gel method were prepared. Polystyrene beads of 100 nm were arrayed orderly on CeO₂ thin films and they were ashed by oxygen plasma for decreasing the size of well-arrayed polystyrene beads. Plasma etching of CeO₂ thin films was performed by inductively coupled plasmas (ICP) with the ashed polystyrene beads as a mask. The high-density nanometer-scaled pillars of CeO₂ were successfully fabricated with a diameter of 50 nm and the distance of 50 nm between the neighboring beads. The effects of the fabrication of CeO₂ nanopillar on the sensing properties were also investigated. The improved sensing properties of CeO₂ for oxygen sensors were obtained after fabrication of nanopillar of CeO₂ by the nanosphere lithography of polystyrene beads. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2007-412-J02003).

EM-Thp12 Influence of Acid Etching of MgAl₂O₄ (111) Substrate on the Deposition of ZnO Thin Film by MOCVD, G.Y. Jhan, Y.J. Chen, H.Y. Lai, J.H. Du, J.H. Liang, National Dong Hwa University, Taiwan

MgAl₂O₄ (111) has lower lattice mismatch than c-plane sapphire with ZnO epilayer, so it is possible for ZnO film deposited on MgAl₂O₄ to obtain better quality than on c-plane sapphire. However, MgAl₂O₄ (111) has two kinds of sublattice of oxygen layer. Although surface energies of two kinds of sublattice of oxygen layer are similar, the sublattice constants of oxygen layers are different. Since the difference of oxygen sublattice constant could affect ZnO film epitaxy quality on MgAl₂O₄ (111), we should control surface of MgAl₂O₄ (111) to expose the proper oxygen sublattices for ZnO film growth. In this research, we studied influence of H₂SO₄ and H₃PO₄ etching of MgAl₂O₄ (111) substrate on the deposition of ZnO thin film by MOCVD. The chemical etching of MgAl₂O₄ was performed with H₂SO₄ and H₃PO₄ respectively to obtain different surfaces of MgAl₂O₄ (111). The ZnO film was deposited on pretreated MgAl₂O₄ (111) at the growth temperature of 350°C. By SEM, XRD and PL analysis, the specimen of H₃PO₄ etching has better quality than specimen of H₂SO₄ etching at the growth temperature of about 350°C. These results imply that different surfaces were created by using H₃PO₄ and H₂SO₄. We proved that ZnO film has good quality on H₃PO₄ etched MgAl₂O₄ (111) substrate.

EM-Thp13 Self-Limiting Growth of Semiconductor Grade Zinc Oxide at Low Temperature by Pulsed Pecvd and Plasma-Enhanced Atomic Layer Deposition, P. Rowlette, C.G. Allen, O. Bromley, D.N. Richards, A. Dubetz, C.A. Wolden, Colorado School of Mines

Self-limiting growth of ZnO was accomplished using both pulsed plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PE-ALD) at temperatures ranging from 25–155 °C. This work explored the suitability of dimethyl zinc (DMZ, Zn(CH₃)₂) as an alternative to the commonly used diethyl zinc (DEZ, Zn(C₂H₅)₂) precursor. Mass spectrometry shows that DMZ is less reactive than DEZ, which may be advantageous for self-limiting growth of semiconductor grade ZnO. In pulsed PECVD DMZ and O₂ were both supplied continuously, while in PE-ALD the DMZ was delivered in pulses separated by purge steps. Films were characterized using spectroscopic ellipsometry, Fourier transform infrared

(FTIR) spectroscopy, photoluminescence (PL), Hall measurements, energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD), atomic force microscopy (AFM), and field emission scanning electron microscopy (FE-SEM). Deposition rates scaled with DMZ exposure during pulsed PECVD films, and could be tuned over a large range (1.5 – 6.0 Å/pulse). The PE-ALD growth rate saturated at 2.9 Å/cycle for DMZ exposures >50 mTorr*s. Deposition rates increased exponentially for pulsed PECVD films as a function of substrate temperature, while PE-ALD displayed a constant rate within a temperature window of 85 to 120 °C. With the substrate temperatures elevated above 70 °C, impurities related to carbon and hydroxyl groups were attenuated below the detection limit of FTIR for both deposition modes. EDS analysis showed that all films were stoichiometric. At low temperatures pulsed PECVD films were amorphous, and became polycrystalline at higher temperatures with a preferred orientation in the (100) direction. PE-ALD produced polycrystalline films with a (100) texture at room temperature, with the preferred orientation switching to the (002) direction as the substrate temperature was increased. Changes in orientation were accompanied by alterations in surface morphology. The as-deposited films were semiconductor grade, with resistivity values ranging from of 1 – 20 W-cm. The high quality of the films was confirmed by strong band edge emission in room temperature PL experiments. Films deposited at room temperature also showed strong emission from oxygen vacancies, however emission from these defects was attenuated for substrate temperatures > 120 °C.

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