ALD Applications
Room On Demand - Session AA14

Emerging:
Optics/Optoelectronics/Metamaterials/Plasmonics

AA14-1 Optical Quantizing Structures in Al_2O_3/TiO_2 Heterostructures by Plasma Enhanced Atomic Layer Deposition, ***Pallabi Paul***, *A. Szeghalmi,* Friedrich Schiller University Jena, Germany

Atomically thin heterostructures and superlattices are promising candidates for various optoelectronic and photonic applications. In this research, different combinations of Al_2O_3/TiO_2 composites are fabricated by plasma enhanced atomic layer deposition (PEALD). The growth, dispersion relation, optical bandgap and composition of such structures are systematically studied by means of UV/VIS spectrophotometry, spectroscopic ellipsometry (SE), x-ray reflectometry (XRR), scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS). Besides, an effective medium approximation (EMA) approach is applied to model the heterostructures theoretically. The refractive index and the indirect bandgap of the heterostructures depend on the ratio of the two oxides, while the bandgap is very sensitive to the thicknesses of the barrier and quantum well layers. A large blue shift of the absorption edge from 400 nm to 320 nm is obtained by changing the TiO_2 (quantum well) thickness from ~ 2 nm to ~ 0.1 nm separated by ~ 2 nm of Al_2O_3 (barrier) layers. PEALD unfolds the possibility of achieving optical quantizing effects within complex heterostructures enabling control of their structures down to atomic scale. It enables a path towards atomic scale processing of new 'artificial' materials with desired refractive indices and bandgap combinations by precise control of their compositions.

Selected compositions are identified for applications in antireflection coatings at 355 nm wavelength. Interference multilayers of TiO_2/Al_2O_3 composites as high refractive index material and SiO_2 as the low refractive index show low reflectance and optical losses at 355 nm wavelength with transmittance values of approximately 99%. Such heterostructures overcome the limitations of the low bandgap dielectric TiO_2 for optical applications in the UV spectral range.

AA14-2 Excellent Surface Passivation of Germanium by ALD Al_2O_3 with a-Si:H Interlayers, ***Willem-Jan Berghuis***, *J. Melskens, B. Macco, R. Theeuwes, K. Erwin,* Eindhoven University of Technology, Netherlands

After the adoption of ALD for the preparation of high-k gate oxides in field-effect transistors (FETs), the unique features of ALD have only become more important with the advancement of the technology nodes: precise and uniform thickness control, excellent conformality, and the ability to generate high-quality surfaces with well-passivated channel surface states. For the next-generation, multiple stacked nanosheet FETs, the requirements become even more stringent. Now the gate needs to be wrapped all around the channel while also both Si and Ge channel surface states need to be passivated. Similar challenges lie in the passivation of Ge and SiGe nanowire devices such as nanolasers, nano-LEDs, and solar cells.

The passivation of SiGe and Ge surfaces by ALD films has been a long-standing challenge which mostly has been addressed by examining FET-like structures. We have recently carried out an in-depth study of the passivation of Ge by ALD Al_2O_3 films. By measuring the carrier lifetime on passivated substrates we extracted the maximum effective surface recombination velocity $S_{eff,max}$. For Al_2O_3, we demonstrated that values as low as $S_{eff,max}$= 170 cm s^{-1} can be achieved after optimization of the ALD substrate temperature, film thickness, and post-deposition anneal temperature. It was moreover established that a GeO_x interlayer forms during ALD and that the GeO_x/Al_2O_3 stack on a Ge surface has a negative fixed oxide charge density (Q_f = - $1.8 \cdot 10^{12}$ cm^{-2}).

In this work, we have systematically examined the surface passivation of Ge by thermal and plasma-enhanced ALD Al_2O_3 in combination with an amorphous silicon (a-Si:H) interlayer. For this purpose, we have grown a-Si:H/Al_2O_3 stacks on Ge substrates under various conditions using plasma-enhanced chemical vapor deposition (PECVD) for the a-Si:H layer (1-10 nm) and ALD for the Al_2O_3 (5-20 nm). We found an excellent surface passivation by an a-Si:H layer as thin as 1.7 nm ($S_{eff,max}$ = 6.8 cm s^{-1}). To better understand the role of the a-Si:H interlayer and its interaction with the ALD Al_2O_3 film, we have performed measurements of the interface defect density (D_{it}) and fixed charge density (Q_f) together with a Transmission Electron Microscopy study. We have found a remarkably high fixed charge (Q_f = - $8.8 \cdot 10^{12}$ cm^{-2}) present in this passivation stack due to the interplay between the Si and PEALD Al_2O_3 leading to a SiO_x interlayer making it a Ge/a-Si:H/SiO_x/Al_2O_3 stack. Thermal ALD Al_2O_3 yields a lower Q_f in comparison, which is likely related to a less prominent SiO_x interlayer. The understanding of this material system is expected to be valuable for the design of well passivated Ge interfaces and devices.

AA14-3 Tunable and Scalable Fabrication of Plasmonic Dimer Arrays With Sub-10 nm Nanogaps by Area Selective ALD, ***Chengwu Zhang***, *B. Willis,* University of Connecticut

Plasmonic nanoantennas, especially with sub-10 nm nanogaps, can greatly enhance electric fields through excitations of surface plasmons, which are collective oscillations of electrons excited by light.Arrays of plasmonic nanoantennas can be designed to concentrate and manipulate light at the nanoscale, and have wide applications such as surface enhanced spectroscopy, photo-driven chemical conversion, and optical information processing.Atomic layer deposition (ALD) is a thin-film deposition technique capable of producing conformal thin films with precise control of thickness and composition at the atomic level.Area selective ALD (AS-ALD) provides a flexible way to precisely tune nanogaps to enhance their optical and electrical properties. In this work, we investigate the optical response of plasmonic nanoantenna dimer arrays with sub-10 nm nanogaps by AS-ALD.

We present a case study of Cu AS-ALD on Pd/Au layered nanoantenna dimers. Figure 1 shows a side view schematic diagram of AS-ALD to tune nanogaps. Pd layers are designed to promote Cu nucleation, and Au layers provide strong plasmonic resonances in the visible and near IR range. Arrays of Pd/Au layered nanoantenna dimers are fabricated on fused quartz substrates using electron beam lithography, followed by Cu AS-ALD to tune the inter-particle distances. Results show nanogaps can be well tuned to sub-10 nm. In figure 2, the nanogaps are measured by electron microscopy and the average post-ALD gap is 6.5 ± 2.2 nm. The inset shows an example dimer with a nanogap of 4.2 nm; each pixel in the SEM image is 0.9 nm. Optical extinction curves were measured to track the changes to the dipolar plasmonic resonances as the number of ALD layers was increased. Figure 3 shows the extinction measurements for light polarized along the axis of the dimer. The dipolar resonance initially blue shifts around 100 nm after 50 ALD cycles, and then red shifts back towards the pre-ALD peak location after more deposition cycles. Control experiments show that the initial blue-shift is largely due to heating, which can slightly modify the nanostructures by rounding corners and edges. Electrodynamics simulations show that additional factors include increasing thickness and decreasing aspect ratio, which also tend to blue-shift the resonances. The data show that beyond 50 cycles, the resonance red-shifts due to the dominant effect of narrowing the nanogaps, which is supported by simulations. In this way, the study shows considerable spectral "tunability" by tailoring the optical responses of plasmonic nanoantenna arrays, while creating nanogaps that concentrate electric fields for various applications.

AA14-4 Lithium Aluminum Fluoride as an Ultraviolet Coating Material, ***John Hennessy***, Jet Propulsion Laboratory

Optical systems operating in the far ultraviolet (90–200 nm) often employ protected aluminum mirror coatings. These mirror systems utilize protective thin films of metal fluoride materials to maintain optical transparency in the wavelength range of interest. The most common protective coating material for this application is MgF_2 which limits the short wavelength performance of the mirror to the band edge cutoff of MgF_2 at approximately 120 nm. There is growing interest for astrophysics applications in the use of LiF protective coatings which can extend the short-wavelength performance due to its larger bandgap, however the hygroscopic properties of LiF can present challenges for the stability and longevity of the final optical system. In this work, we investigate the use of atomic layer deposition to create thin films of lithium aluminum fluoride as an ultraviolet coating material. We have employed a supercycle approach utilizing LiHMDS, tris(dimethylamino)aluminum, and anhydrous HF as co-reactants at substrate temperatures between 100 and 200 °C. This chemical pathway avoids possible deleterious interactions that can occur between simple alkylaluminum precursors and alkali materials, and ultimately allows for arbitrary mixed thin film compositions ranging from purely crystalline LiF, to purely amorphous AlF_3. At intermediate supercyle ratios we also show that crystalline films of Li_3AlF_6 can be deposited with this process as confirmed by x-ray diffraction analysis. We present recent results on protected aluminum mirror coatings fabricated with this approach, along with environmental exposure testing comparing the performance of Li_3AlF_6 to LiF and AlF_3. The prospects for utilizing this approach in future NASA instrumentation will be discussed along with the

possibility of using these films as battery coating materials. Crystalline films of Li_3AlF_6 are also known to possess moderate Li-ion conductivity and the low deposition temperature investigated in this work may have benefits over other ALD approaches in this material system.

AA14-7 Stress Compensated HfO_2/SiO_2 High-reflective Coatings at 355 nm and 532 nm by Plasma Enhanced Atomic Layer Deposition using Substrate Biasing, ***Vivek Beladiya,*** Friedrich-Schiller-University Jena, Germany*; D. Kästner,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany*; S. Riese, P. Hanke,* LAYERTEC GmbH, Germany*; A. Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany

Atomic layer deposition is a promising thin film deposition technology due to its ability to coat complex formed substrates with precise thickness control and excellent uniformity. The substrate biasing technique in plasma enhanced atomic layer deposition has recently gained attention due to its ability to manipulate material properties such as refractive index, density, residual OH impurity, residual mechanical stress, crystallinity, and surface roughness. The kinetic energy of the plasma species can be varied by applying a substrate bias potential across the plasma sheath at the substrate surface. In this work, we have deposited high-reflective (HR) coatings at 355 nm and 532 nm at 100°C deposition temperature using substrate biasing.

The multilayer system consists of HfO_2 and SiO_2 as a high and low refractive index layer, respectively, which were grown using a substrate biasing. The total film thickness of HR@355nm and HR@532nm were 1.6 µm and 2.3 µm, respectively. The total residual stress measured on double-side polished Si wafers was 76 MPa (tensile) and 112 MPa (tensile) for HR@355nm and HR@532 nm, respectively. The reflectance of 99.9 was measured using a spectrophotometer at 355 nm and 532 nm wavelengths for HR@355nm and HR532nm, respectively.Additionally, a reflectance of above 99.9 was determined at 355 nm wavelength for HR@355nm multilayer coating by means of cavity ring-down measurements. The coatings were free of delamination and visible cracks. The laser-induced damage threshold (LIDT) was performed at 355 nm using the R-on-1 method on HR@355nm multilayer coating. The LIDT of 19 J/cm³ was observed. Hence, we have successfully demonstrated stress compensated high-reflective (HR) coatings for the designed wavelengths of 355 nm and 532 nm with excellent uniformity and mechanical stability.

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