1) Atomically smooth and single crystalline Ge(111)/cubic-Pr₂O₃(111)/Si(111) heterostructures: Structural and chemical composition study

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**Abstract:** Engineered wafer systems are an important materials science approach to achieve the global integration of single crystalline Ge layers on the Si platform. Here, we report the formation of single crystalline, fully relaxed Ge(111) films by molecular beam epitaxial overgrowth of cubic Pr oxide buffers on Si(111) substrates. Reflection high-energy electron diffraction, scanning electron microscopy, and x-ray reflectivity show that the Ge epilayer is closed, flat, and has a sharp interface with the underlying oxide template. Synchrotron radiation grazing incidence x-ray diffraction and transmission electron microscopy reveal the type-A/B/A epitaxial relationship of the Ge(111)/cubic Pr₂O₃(111)/Si(111) heterostructure, a result also corroborated by theoretical ab initio structure calculations. Secondary ion mass spectroscopy confirms the absence of Pr and Si impurities in the Ge(111) epilayer, even after an annealing at 825 °C.

2) Structure and defects of epitaxial Si(111) layers on Y₂O₃(111)/Si(111) support systems

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**Abstract:** Single crystalline epitaxial Si(111) / $Y_2O_3(111)$ / Si(111) heterostructures were grown by molecular beam epitaxy and the morphology, structure, and defects were characterized in detail. The growth of a closed and smooth layer system is demonstrated by means of reflection high energy electron diffraction measurements. X-ray reflectometry and high resolution Rutherford backscattering (RBS) experiments show low surface and interface roughnesses. Channeling RBS as well as x-ray diffraction pole figure studies demonstrate the type A/B/A epitaxy relationship of the Si(111) / $Y_2O_3(111)$ / Si(111) heterostructure and reveal the existence of defects in the epitaxial Si(111) layer. These defects are studied in detail with high resolution transmission electron microscopy, disclosing microtwin formation and type B Si grains as the major defects.

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**3) On the band gaps and electronic structure of thin single crystalline praseodymium oxide layers on Si(111)**

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**Abstract:** The influence of stoichiometry and crystal structure on the electronic properties of single crystalline cubic PrO$_2$(111), cubic Pr$_2$O$_3$(111), and hexagonal Pr$_2$O$_3$(0001) thin film heterostructures on Si(111) was investigated by synchrotron radiation based photoemission electron spectroscopy (PES) and x-ray absorption spectroscopy (XAS). A detailed analysis of the complex satellite structures of PES Pr 3d lines of the various Pr oxide phases is given. PES was in addition applied to study the O 2p derived valence band structure and the positions of the occupied Pr 4f state density. It is found by a combined PES-XAS study that especially the band gap values strongly depend on the stoichiometry and crystal structure of the single crystalline Pr oxide layer. Furthermore, the close structure relationship between cubic Pr$_2$O$_3$(111) and PrO$_2$(111) films is probably the reason for the detection of nonstoichiometric behavior, an effect which is far less pronounced in case of hexagonal Pr$_2$O$_3$(0001) layers. A possible origin of this effect is given by a surface modified valence change and therefore of importance to understand in future the epitaxial overgrowth of these oxide buffer heterostructures by alternative semiconductors such as germanium.
4) Engineered Si wafers: On the role of oxide heterostructures as buffers for the integration of alternative semiconductors

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Abstract: Engineered Si wafer systems present an important materials science approach to further improve the performance of Sibased micro- and nanoelectronics. This is due to the potential to integrate alternative semiconductor layers on the mature Si wafer technology platform which are otherwise too expensive or even impossible to grow in bulk form in the required quality and quantity. Ge is attracting increasing research interest because it is for example a promising material for high mobility channel CMOS technologies as well as a mediator material to achieve the manufacturing of III-V/Si hybrid devices. The integration of Ge on Si wafers is today either achieved by a combination of layer transfer and wafer bonding techniques or by a sequence of subsequent, epitaxial thin film deposition growth steps. In the latter case, the traditional approach to integrate Ge layers of low defect densities is given by the use of compositionally graded SiGe heterostructures. As this approach suffers however from required SiGe buffer thicknesses on the micrometer scale, making integrated circuit processing difficult, research on the development of innovative buffer heteroepitaxy approaches is intensively pursued. A new interesting class of buffer materials with a high degree of flexibility is given by oxide heterostructures. Using the integration of single crystalline Si and Ge on the Si(111) material platform via oxide heterostructures as an example, the flexibility of engineered oxide heterostructures to control important epitaxy parameters is demonstrated. In this study, epitaxial Si(111) and Ge(111) layers were grown on cubic Y2O3(111)/cubic Pr2O3(111)/Si(111) and Pr2O3(111)/Si(111) support systems, respectively. The structural properties of the Si-on-Insulator (SOI) and Ge-on-Insulator (GOI) heterostructures were characterized in detail by a combination of laboratory- and synchrotron-based methods. As main result, both the epitaxial Si(111) and Ge(111) films were shown to be atomically smooth and single crystalline (i.e. free of stacking twins). Defect engineering approaches need to be applied in future to reduce stacking faults (e.g. microtwins) which are identified as the major defect mechanism in the epitaxial Si(111) and Ge(111) films.

5) Ge integration on Si via rare earth oxide buffers: From MBE to CVD

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**Abstract:** Single crystalline rare earth oxide heterostructures are flexible buffer systems to achieve the monolithic integration of Ge thin film structures on Si. The development of engineered oxide systems suitable for mass-production compatible CVD processes is hereby of special importance. In this paper, the interaction of Ge with PrO$_2$(111)/Si(111) heterostructures is studied in detail to achieve this goal. MBE based in situ growth studies unveil the chemical reduction of the PrO$_2$ buffer during the initial Ge deposition, the occurrence of a Volmer Weber growth mode of Ge on the resulting Pr$_2$O$_3$ heterostructure and the final formation of single crystalline, atomically smooth and c(2 x 8) reconstructed Ge(111) film structures. Comparative CVD Ge heteroepitaxy studies on MBE grown PrO$_2$(111)/Si(111) and Pr$_2$O$_3$(111)/Si(111) buffer systems indicate that the highly reactive lattice oxygen of PrO$_2$ plays an active role to avoid during initial exposure to the reducing ambient of the GeH$_4$ precursor chemistry the decomposition of the oxide buffer system.

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6) **Postdeposition annealing induced transition from hexagonal Pr$_2$O$_3$ to cubic PrO$_2$ films on Si(111)**

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**Abstract:** Films of hexagonal praseodymium sesquioxide (h-Pr$_2$O$_3$) were deposited on Si(111) by molecular beam epitaxy and thereafter annealed in 1 atm oxygen at different temperatures, ranging from 100 to 700 °C. The films of the samples annealed at 300 °C or more were transformed to PrO$_2$ with B-oriented Fm$\overline{3}$m structure, while films annealed at lower temperatures kept the hexagonal structure. The films are composed of PrO$_2$ and PrO$_2$-d species, which coexist laterally and are tetragonally distorted due to the interaction at the interface between oxide film and Si substrate. Compared to PrO$_2$, PrO$_2$-d has the same cubic structure but with oxygen vacancies. The oxygen vacancies are partly ordered and increase the vertical lattice constant of the film, whereas the lateral lattice constant is almost identical for both species and on all samples. The latter lattice constant matches the lattice constant of the originally crystallized hexagonal praseodymium sesquioxide. That means that no long range reordering of the praseodymium atoms takes place during the phase transformation. © 2009 American Institute of Physics.

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7) **Growth of praseodymium oxide on Si(111) under oxygen-deficient conditions**

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Abstract: Surface science studies of thin praseodymium oxide films grown on silicon substrates are of high interest in view of applications in such different fields as microelectronics and heterogeneous catalysis. In particular, a detailed characterization of the growth and the final structure of the films are mandatory to achieve a fundamental understanding of such topics as oxygen mobility and defect structure, and their role for the electronic and chemical properties. In this paper, the MBE growth of praseodymium oxide films on Si(111) substrates was investigated at low-deposition rates (0.06 nm/min) and low-oxygen partial pressures ($p(O_2) < 1 \times 10^{-10}$ mbar). To obtain insight into the structure and chemical composition of the growing film, spot profile analyzing low-energy electron diffraction (SPA-LEED), transmission electron microscopy, and synchrotron radiation-based x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) were applied. SPA-LEED reveals the formation of an initial closed layer followed by continuous roughening and formation of ordered three-dimensional structures. This result is in contrast to observations at higher-deposition rates, were a layer-by-layer growth was reported. XAS and XPS provide evidence that a continuous reaction takes place in the growing Pr$_2$O$_3$ film leading to the formation of silicate and silicide structures within the film. Combining all data, a consistent picture of the deposition of praseodymium oxide on Si(111) emerges which clearly shows that in contrast to higher-throughput molecular beam epitaxy conditions the reactivity of the growing film strongly influences the growth behavior at low-deposition rates and low pressures.

8) X-ray characterization of epi-Ge/Pr$_2$O$_3$/Si(111) layer stacks by pole figures and reciprocal space mapping

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Abstract: An epi-Ge/Pr$_2$O$_3$/Si(111) layer structure prepared by consecutive steps of epitaxial deposition and annealing is used to demonstrate the possibility of a complex characterization by combination of different X-ray diffraction techniques. Especially pole figure measurements, reciprocal space mapping (RSM) and high resolution (HR) $\Theta/2\Theta$ scans at selected inclined netplanes were successfully used to determine the inplane lattice orientation of the layers relative to the substrate, the strain state of all layers and the structural perfection of the epi-Ge film. It was found that the major part of the epi-Ge layer has the same type A
stacking orientation as the Si substrate, but about 0.6% is of type B. The Pr2O3 buffer layer exhibits type B only. The strain state of oxide and epi-Ge was determined, and a small difference in the lattice constant of type A and B epi-Ge was found. Microwtins lying in inclined {111} planes were unambiguously identified by pole figure measurements as the dominating structural defects in the epi-Ge layer. They cause a characteristic scattering pattern in reciprocal space maps. The proposed combination of X-ray techniques allows a relatively fast, integral and non-destructive analysis of heteroepitaxial semiconductor oxide semiconductor structures.

9) Defect structure of Ge(111)/cubic Pr2O3(111)/Si(111) heterostructures: Thickness and annealing dependence

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Abstract: The defect structure of Ge(111) epilayers grown by molecular beam epitaxy on cubic Pr2O3(111)/Si(111) support systems was investigated by means of transmission electron microscopy and laboratory-based x-ray diffraction techniques. Three main types of defects were identified, namely, rotation twins, microtwins, and stacking faults, and studied as a function of Ge film thickness and after annealing at 825 °C in ultrahigh vacuum. Rotation twins were found to be localized at the Ge(111)/cubic Pr2O3(111) interface and their amount could be lowered by the thermal treatment. Microtwins across {111} were detected only in closed Ge films, after Ge island coalescence. The fraction of Ge film volume affected by microtwinning is constant within the thickness range of ~20–260 nm. Beyond 260 nm, the density of microtwins is clearly reduced, resulting in thick layers with a top part of higher crystalline quality. Microtwins resulted insensitive to the postdeposition annealing. Instead, the density of stacking faults across {111} planes decreases with the thermal treatment. In conclusion, the defect density was proved to diminish with increasing Ge thickness and after annealing. Moreover, it is noteworthy that the annealing generates a tetragonal distortion in the Ge films, which get in-plane tensely strained, probably due to thermal mismatch between Ge and Si.

10) Synchrotron x-ray characterization of structural defects in epi-Ge/Pr2O3/Si(111) layer stacks

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Abstract: Epi-Ge/Pr$_2$O$_3$/Si(1 1 1) layer structures were studied by synchrotron grazing incidence diffraction to analyse the structural perfection of the top epi-Ge and the oxide buffer layer independently. The dominating features for the epi-Ge layer are pronounced streaks of diffuse scattering in the <1 1 1> directions that are caused by microtwins and stacking faults lying in the {1 1 1} glide planes 70.5° tilted to the wafer surface. It is confirmed that grains of type B orientation in the epi-Ge layer are located near the oxide–Ge interface only. The few nanometres thick Pr$_2$O$_3$ buffer layer shows similar streaks of diffuse scattering indicating a high concentration of structural defects in the tilted {111} planes. The relatively poor crystallographic quality of the oxide layer with an in-plane domain size of about 35 nm, a mosaicity of 0.7° and a strain variation of 0.8% is discussed as a possible reason for structural imperfections in the upper epi-Ge layer. Measurements on samples with different epi-Ge thicknesses show that the epi-Ge layer has no influence on the strain state of the Pr$_2$O$_3$ buffer layer.

11) A complex x-ray structure characterization of Ge thin film heterostructures integrated on Si(001) by aspect ratio trapping and epitaxial lateral overgrowth selective chemical vapor deposition techniques

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Abstract: The development of Ge thin film substrates with low defect densities is of interest for future microelectronics as well as photovoltaics. This paper presents a complex x-ray characterization of Ge heterostructures, which were integrated on patterned Si(001) substrates using “aspect ratio trapping (ART)” and “epitaxial lateral overgrowth (ELO).” In both cases, thermal SiO$_2$ layers were patterned into trenches with appropriate aspect ratio to confine misfit dislocations. In the case of ART Ge thin films grown in 180 nm spaced trenches, the x-ray characterization reveals that the Ge coalescence process between neighboring growth windows must be carefully controlled to avoid defect generation. In the case of ELO Ge heterostructures grown from trenches spaced by 20 µm, coalescence effects are clearly reduced but complications are detected in the form of lattice plane tilt in the ELO wings. Simulations are applied to unveil the influence of the different thermal expansion coefficients of Ge, Si, and SiO$_2$ on the strain status of the ART and ELO Ge heterostructures.

12) Dielectric properties of single crystalline PrO$_2$(111)/Si(111) heterostructures: Amorphous interface and electrical instabilities


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Abstract: Single crystalline PrO$_2$(111)/Si(111) heterostructures are flexible buffers for global Ge integration on Si. A combined materials science–electrical characterization is carried out to study the influence of postdeposition annealing in 1 bar oxygen at 300–600 °C on the dielectric properties of PrO$_2$(111)/Si(111). The materials science transmission electron microscopy and x-ray reflectometry studies reveal that postdeposition oxidation of the PrO$_2$(111)/Si(111) boundary results in an amorphous interface (IF) layer, which grows in thickness with temperature. Nondestructive depth profiling synchrotron radiation-based x-ray photoelectron spectroscopy and x-ray absorption spectroscopy methods demonstrate that this amorphous IF layer is composed of two Pr-silicate phases, namely, with increasing distance from Si, a SiO$_2$-rich and a SiO$_2$-poor Pr silicate. The electronic band offset diagram shows that the wide band gap dielectric Pr silicate results in higher band offsets with respect to Si than the medium band gap dielectric PrO$_2$. The electrical characterization studies by C-V measurements show that (a) well-behaved dielectric properties of the PrO$_2$(111)/IF/Si(111) are achieved in a narrow postdeposition oxidation window of 400–450 °C and that (b) defects are distributed over the Pr-silicate IF layer. Temperature-dependent J-V studies report furthermore that the formation of the single crystalline PrO$_2$/amorphous Pr-silicate bilayer structure on Si(111) results in (a) improved insulating properties and (b) strong electrical instability phenomena in the form of a Maxwell–Wagner instability and dielectric relaxation.
1) The role of the HfO$_2$–TiN interface in capacitance–voltage nonlinearity of Metal-Insulator-Metal capacitors

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**Abstract:** The high-k Metal-Insulator-Metal (MIM) capacitor Back-End-of-Line (BEOL) integration into mixed signal and Radio Frequency (RF) circuits is characterized by the effort toward optimizing the capacitance voltage linearity. This letter is focused on the role of the TiO$_x$N$_y$-based interfacial layer with respect to Capacitance–Voltage $C(V)$ curves of Au/HfO$_2$/TiN MIM capacitors. The correlation between the quadratic capacitance–voltage variation and interfacial layer thickness is demonstrated. The quadratic voltage coefficient of the dielectric stack can be reduced by increasing the thickness of the TiO$_x$N$_y$ layer.

2) Influence of the electrode material on HfO$_2$ metal-insulator-metal capacitors

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**Abstract:** TaN and TiN are investigated as bottom electrode materials for metal-insulator-metal (MIM) capacitor applications. Atomic vapor deposited HfO$_2$ films are used as high-k dielectric. The influence of the interfacial layer between HfO$_2$ and the bottom electrode on the electrical performance of MIM capacitors is evaluated. The capacitance density as well as the capacitance voltage linearity of high-k MIM capacitors is affected by the electrode material. There is also an impact by TaN and TiN on leakage current density and breakdown strength of the devices.
3) Thermal oxidation of chemical vapour deposited tungsten layers on silicon substrates for embedded non-volatile memory application

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Abstract: This research is targeted to enhance the functionality of bipolar complementary metal-oxide-semiconductor by innovative concepts of embedded resistive random access memory (RRAM) cells integration in the backend-of-line (BEOL) region. The material of our interest is tungsten oxide as an insulator in RRAM cells and we focussed on the growth and characterisation of closed tungsten oxide layers. In this materials science study, we investigated the tungsten oxidation process under BEOL constraints (<450 °C). Thin films of tungsten oxide (6–50 nm) were prepared by oxidising, under an atmosphere of one bar oxygen, the chemical vapour deposited tungsten layers on TiN covered silicon wafers. The X-ray photoelectron spectroscopy investigations indicate that the stoichiometric WO$_3$ grows after oxidation at 300 °C for an hour. The tungsten oxide layers prepared above 300 °C for longer than 15 min were non-stoichiometric. The X-ray diffraction investigations reveal the crystallisation of the WO$_3$ layers in monoclinic phase above 350 °C when oxidised for longer than 30 min; above 400 °C the (001) growth texture becomes dominant.

4) Pulse-induced low-power resistive switching in HfO$_2$ metal-insulator-metal diodes for nonvolatile memory applications

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Abstract: The conduction process as well as the unipolar resistive switching behavior of Au/HfO$_2$ /TiN metal-insulator-metal structures were investigated for future nonvolatile memory applications. With current-voltage measurements performed at different temperatures (200–400 K), the Poole–Frenkel effect as conduction process was identified. In particular, we extracted a trap energy level at $\Phi_{ti}$ =0.35+0.05 eV below the HfO$_2$ conduction band to which a microscopic origin is tentatively assigned. From current-voltage measurements of Au/HfO$_2$ /TiN structures, low-power (as low as 120 µW) resistive switching was observed. The required forming process is shown to be an energy-induced phenomenon. The characteristics include electric pulse-induced resistive switching by applying pulses up to 100 µs and a retention time upon continuous nondestructive readout of more than $10^4$ s.
5) Band alignment and electron traps in Y$_2$O$_3$ layers on (100)Si

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**Abstract:** Y$_2$O$_3$ films deposited by atomic vapor deposition on (100)Si with a 2 or 5 nm thick pregrown thermal SiO2 are investigated as possible charge trapping layers. Analysis of these structures using spectroscopic ellipsometry, photoconductivity, and internal photoemission reveals that Y$_2$O$_3$ has a 5.6 eV wide optical bandgap and a 2.0 eV conduction band offset with silicon. Photo(dis)charging experiments show that the optical energy depth of most of the traps exceeds 1.5 eV with respect to the Y$_2$O$_3$ conduction band, explaining the observed charge retention time of $\sim 10^8$ s at room temperature, even in the absence of a blocking insulator.