Sofja Kovalevskaja-Programm

A short description of scientific results

obtained by

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April 2004

The reserarch work can be devided in five topics:

a) Investigations of the plasma chemistry:

b) Role of impurities on the elastic properties:

c) Processing – structure – property – reationships:

d) Nanolaminates: Structure – property – relationships

e) Quantum design of a B-O-Y phase

a) Investigations of the plasma chemistry:

a1) We describe the temporal development of the plasma composition in a pulsed plasma stream generated by cathodic arc. Cathodes of Zr and Cr were operated at various nitrogen pressures. The time-resolved plasma composition for the cathode materials was analyzed with time-of-flight charge-to-mass spectrometry, and was found to be a strong function of the nitrogen pressure. Large plasma composition gradients were detected within the first 60 ms of the pulse, the nitrogen ion concentration increasing with increasing pressure. The results are explained by the formation and erosion of a compound layer formed at the cathode surface in the presence of a reactive gas. The average charge state was also found to be affected by the reactive gas pressure as well as by the time after ignition. The charge states were highest in the beginning of the pulse at low nitrogen pressure, decreasing to a steady-state value at higher pressure. These results are of importance for reactive plasma processing and for controlling the evolution of thin film composition and microstructure.

More information can be found in: J. Rosen, A. Anders, L. Hultman and **J. M. Schneider**: Temporal development of the composition of Zr and Cr cathodic arc plasma stream in a N2 environment, *Journal of Applied Physics* 94 (3) (2003) 1414.

a2) The species and ion charge state evolution of a pulsed cathodic arc plasma was investigated at different pressures. A zirconium cathode was operated in a nitrogen environment, and the plasma composition was analysed by time-of-flight charge-to-mass spectrometry. Large plasma chemistry changes were detected with respect to time and pressure. The 250 μs plasma pulse can be divided in two characteristic phases: a transient phase before 150 μs and a steady state phase for all later times. The measured changes in plasma chemistry in the transient phase at $p \sim 10^{-5}$ Torr are explained by metal ion-gas charge transfer, while the increasing N^+ concentration in the $p > 10^{-5}$ Torr range most likely originates from erosion of the nitrided cathode surface. In the steady state phase, a pressure-induced change from higher to lower charge states was observed, which is likely due to three-body recombination. These results are of importance for understanding the evolution of thin film composition and microstructure during reactive plasma deposition.

More information can be found in: J. Rosen, A. Anders, L. Hultman and **J. M. Schneider**: Charge state and time resolved plasma composition of a pulsed zirconium arc in a nitrogen environment, submitted to *Journal of Applied Physics* 2004

b) Role of impurities on the elastic properties:

b1) Boron suboxide thin films, with controlled carbon content, were grown by RF dual magnetron sputtering of boron and carbon targets in an argon-oxygen atmosphere. Film composition, structure, mechanical, and electrical properties were evaluated with x-ray photoelectron spectroscopy, Auger electron spectroscopy, x-ray diffraction, transmission electron microscopy, nanoindentation, and high-frequency capacitance-voltage measurements. X-ray amorphous B-O-C films (O/B=0.02) showed an increase in density from 2.0 to 2.4 g/cm3 as C content was increased from 0 to 0.6 at.% and the film with the highest density had nano-crystalline inclusions. The density increase occurred most likely due to the formation of B-C bonds, which are shorter than B-B bonds. All measured material properties were found to depend strongly on the C content and thus film density. The elastic modulus increased from 188 to 281 GPa with the increasing C content, while the relative dielectric constant decreased from 19.2 to 0.9. Hence, B-O-C films show a potential for protective coatings and even for application in electronic and optical devices.

More information can be found in: D. Music, V. Kugler, Z. Cigany, A. Fink, O. Werner, **J.M. Schneider**, L. Hultman and U. Helmersson, The role of carbon in boron suboxide thin films, *Journal of Vacuum Science and Technology A* 21 (2003) 1355.

c) Processing – structure – property – reationships:

c1) Boron suboxide thin films have been deposited on Si(100) substrates by reactive RF magnetron sputtering of a sintered B target in an Ar/O_2 atmosphere. Elastic recoil detection analysis was applied to determine the film composition and density. Film structure was studied by X-ray diffraction and transmission electron microscopy. The elastic modulus, measured by nanoindentation, was found to decrease as the film density decreased. The relationship was affected by tuning the negative substrate bias potential and the substrate temperature during film growth. A decrease in film density, by a factor of 1.55, caused an elastic modulus reduction by a factor of 4.5, most likely due to formation of nano-pores containing Ar. It appears evident that the large scattering in the published data on elastic properties of films with identical chemical composition can readily be understood by density variations. These results are important for understanding the elastic properties of boron suboxide, but may also be qualitatively relevant for other B-based material systems.

More information can be found in: D. Music, U. Kreisig, Z Czigany, U. Helmersson and **J.M. Schneider**, Elastic modulus-density relationship for amorphous boron suboxide thin films, *Applied Physics A*, A76 (2003) 269.

c2) BCN films were deposited by plasma enhanced chemical vapour deposition (PECVD) from chloridic precursors in an industrial-scale d.c. plasma CVD plant, where the power density (pd) at the substrate was varied, and the as deposited films were analysed with respect to composition, structure and elastic properties. We find, independent of the power density applied to the substrate, evidence for sp2 coordinated boron which is consistent with the formation of a hexagonal or a rhombohedral BCN. Based on electron microscopy and electron diffraction we suggest a change in film texture from an orientation where the c-axis is parallel to the substrate surface at pd=0.5 W/cm^2 to more randomly oriented a polycrystalline structure at pd=2 W/cm^2. As the power density was increased a reduction in compressive stress was measured which may be a consequence of defect annihilation and subsequent relaxation. Furthermore, the texture-stress relationship suggested here is consistent with published thermodynamic calculations. The elastic modulus decreases from 115 to 40 GPa as the power density at the substrate is increased. This can be understood by the suggested change in texture as a consequence of the large elastic anisotropy of sp2 coordinated BCN.

More information can be found in: D. Kurapov, D. Neuschütz, R. Cremer, T. Pedersen, M. Wuttig, D. Dietrich, G. Marx and **J.M. Schneider**, Synthesis and mechanical properties of BCN coatings deposited by PECVD, *Vacuum 68 (2003)335*.

c3) C-free boron suboxide, BOx, thin films have been deposited on Si(100) by reactive RF magnetron sputtering of B powders in an Ar/O_2 atmosphere. Elastic recoil detection analysis and x-ray diffraction were used to study the influence of the O incorporation on the film composition and structure and relate them to mechanical properties, which were evaluated by nanoindentation. As x in BO_x was increased from 0.08 to 0.18, the elastic modulus of the x-ray amorphous films decreased from 273 to 231 GPa, by 15%. This can be understood using classical molecular dynamics (MD) with a Buckingham-like interaction potential: The increase in the O concentration and corresponding formation of B-O bonds, shown to be longer than the B-B bonds, resulted in larger ionic contributions as well as a density reduction. This increased ionicity was responsible for the observed decrease in elastic modulus. As even more O was incorporated (x>0.18), the H concentration increased, exceeding 0.3 at.%. This may cause the formation of boric acid (H_3BO_3) as a result of the chemical reaction with H_2O upon atmosphere exposure. The presence of van der Waals and hydrogen bonding, associated with H_3BO_3 formation, provides a reasonable explanation for the extensive decrease in elastic modulus from 231 to 15 GPa, by 94%. The new parameterization for the Buckingham-like interaction potential, introduced in this study, can be used for MD simulations of amorphous BOx systems without H_3BO_3.

More information can be found in: D. Music, U. Kreisig, V. Chirita, **J.M. Schneider** and U. Helmersson, Elasic modulus of amorphous boron suboxide thin films sudied by theoretical and experimental methods, *Journal of Applied Physics, 93 (2003) 940*.

c4) The surface reactivity of $\alpha\text{-}Al_2O_3$ (0001) has been investigated theoretically using Density Functional Theory. The adsorption process of $Al1^+$, Al^{2+}, Al^{3+} and O^+ were studied in order to identify possible preferential adsorption sites during thin film growth. Differences in near surface atomic displacements (e.g. adsorption-induced surface reconstructions), energies and bonding character have been evaluated. The adsorption energies for the metallic ions showed a strong dependence on both initial charge and adsorption site. The O^+ ions showed no site dependence, but adsorption energies similar to those

calculated for $Al1^+$. The results indicate that the adsorption of O^+ and $Al3^+$ may favour the formation of an amorphous structure, which is consistent with experimental observations. The results are of fundamental importance for the understanding of thin film microstructure evolution.

More information can be found in: J. Rosen, **J.M. Schneider** and K. Larsson, Thin film growth related adsorption study of Al and O ions on an α-Al2O3 surface, submitted to *Journal of Physical Chemistry B*, 2004

d) Nanolaminates: Structure – property – relationships

d1) We have performed theoretical studies of the bulk modulus of M2AlC, where M5Ti, V, Cr by means of ab initio total energy calculations using the projector augmented wave methods. Our estimated equilibrium volume and the lattice parameters (c/a) agree well (within 2% and 0.06%, respectively) with experimental data. The bulk modulus of M_2AlC increases as Ti is substituted with V and Cr by 19% and 36%, respectively. This can be understood since the substitution of Ti by V and Cr is associated with an extensive increase in the M–Al and M–C bond energy.

More information can be found in: Z. Sun, R. Ahuja, S. Li, **J.M. Schneider**: Structure and bulk modulus of M_2AlC (M=Ti, V and Cr), Applied Physics Letters 83 (2003) 899.

d2) We have performed theoretical studies of the solubility within $(M'_xM_{2-x})AlC$, where M' and M={Ti, V, and Cr} by means of ab initio total energy calculations. The theoretical values of equilibrium volume and the optimized c/a ratios are in good agreement with those of experiments (within ± 4% and ± 1.3%, respectively). Furthermore we show that if x is increased from 0 to 2 the bulk modulus can be increased by as much as 36%. Based on the total density of states analysis as well as the energy of formation, we suggest that the investigated systems show solubility except for the $(Cr,Ti)_2AlC$ system. This conclusion is consistent with the published work where solubility within the system $(V,M)_2AlC$, (M=Ti and Cr) as well as a miscibility gap in the system $(Cr,Ti)_2AlC$ were experimentally observed [Schuster et al., J. Solid State Chem. 32, 213 (1980)].

More information can be found in: Z. Sun, R. Ahuja and J.M. Schneider: Theoretical investigation of the solubility in (M'M2-x)AlC (M' and M= Ti, V, Cr), *Phys. Rev. B* 68, 224112 (2003).

d3) M_2AlC phases, where M is a transition metal, are layered ternary compounds that possess unusual properties. In this paper, we have calculated the elastic properties of M_2AlC, with M = Ti, V, Cr, Nb and Ta, by means of ab initio total energy calculations using the projector augmented-wave method. We have derived the bulk and shear moduli, Young's moduli and Poisson's ratio for ideal polycrystalline M_2AlC aggregates. We have estimated the elastic modulus of Cr_2AlC with 357.7 GPa while the values of all other phases are in the range 309 ± 10 GPa. We suggest that this can be understood based on the calculated bond energies for the M–C bonds. Furthermore, our results indicate a profound elastic anisotropy of M_2AlC even compared to materials with a well-established anisotropic

character such as a-alumina. Finally, we have estimated the Debye temperatures of M_2AlC from the average sound velocity.

More information can be found in: Z. Sun, S. Li, R. Ahuja and **J.M. Schneider**: Calculated elastic properties of M2AlC (M = Ti, V, Cr, Nb and Ta), *Solid State Communications* 129 (2004) 589-592.

d4) We have calculated the equilibrium volume and the density of states (DOS) of Cr_2AlC for antiferromagnetic (AFM), ferromagnetic (FM) and paramagnetic (PM) configurations by ab initio total energy calculations. Based on a comparison of the cohesive energies as well as the DOS for all three magnetic configurations we have identified the FM configuration to be metastable. Furthermore, we report the structural characterization of polycrystalline Cr_2AlC thin films grown by magnetron sputtering. Our calculated interplanar distances and equilibrium volume for the PM and AFM configurations are in good agreement with our experiment. The charge density distribution suggests that the chemical bonding between Cr and C in Cr_2AlC is very similar to the one in cubic CrC.

More information can be found in: **J.M. Schneider** Z. Sun, R. Mertens, F. Uestel and R. Ahuja: Ab initio calculations and experimental determination of the structure of Cr_2AlC, *Solid State Communications*, in press (2004)

d5) We have investigated the elastic properties of nanolayered M2AC with M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and A=Al, Ga, Ge, Sn by ab initio calculations. We suggest that M2AC can be classified into two groups: One where the bulk modulus of the binary MC is conserved and another group where the bulk modulus is decreased. This classification can be understood in terms of coupling between MC and A layers which is defined by the valence electron population. These results may have implications for the understanding of properties and performance of this class of solids.

More information can be found in: Z. Sun, D. Music, R. Ahuja, S. Li, and **J. M. Schneider**: Bonding and classification of nanolayered ternary carbides, submitted to *Phys. Rev. B* 2004

d6) Using ab initio calculations, we have studied 20 boron based perovskites (RM_3B, where R and M are rare earth and 4d metals, respectively). We show that the coupling of interleaved M – R

with M – B layers can be switched from predominantly covalent-ionic to metallic in character by varying the population of the M d-shells. Based on these calculations, we predict the coexistence of covalent-ionic and metallic bonding in these compounds giving rise to an unusual combination of properties.

More information can be found in: Denis Music, Zhimei Sun, and **Jochen M. Schneider**: Coupling in perovskite boride nanolaminates, submitted to *Physical Review Letters*, 2004

e) Quantum design of a B-O-Y phase

e1) Ab initio calculations are used to design a crystalline boron–oxygen–yttrium BOY phase. The essential constituent is yttrium substituting for oxygen in the boron suboxide structure ($BO_{0.17}$) with Y/B and O/B ratios of 0.07. The calculations predict that the BOY phase is 0.36 eV/atom more stable than crystalline $BO_{0.17}$ and experiments confirm the formation of crystalline thin films. The BOY phase was synthesized with reactive rf magnetron sputtering and identified with x-ray and selected area electron diffraction. Films with Y/B ratios ranging from 0.10 to 0.32, as determined via elastic recoil detection analysis, were grown over a wide range of temperatures (300–600°C) and found to withstand 1000 °C.

More information can be found in: D. Music, V. Chirita, U. Kreissig, Zs. Czigany, **J.M. Schneider**, U. Helmersson: Quantum design and synthesis of a boron-oxygen-yttrium phase, *Applied Physics Letters* 82 (2003) 4286.

e2) The effect of chemical composition on the elastic and electrical properties is studied for the BO_xY_z system with $0.27<x<1.14$ and $0.36<z<0.08$. We use ab initio calculations to obtain the elastic constants and density of states for $BO_{1.5}$ and the BOY phase (yttrium substituting for oxygen in the boron suboxide structure). For decreasing x values, the elastic modulus is predicted to increase from 11 to 340 GPa, while electronic structure calculations suggest a shift in electrical properties from insulating to metallic. Thin films in the B-O-Y system are grown by reactive rf magnetron sputtering. As x decreases from 1.14 to 0.27, the elastic modulus increases from 12 to 282 GPa, which is a factor of 24, while resistivity decreases from 7.6 ± 0.4 to (3.8 ± 0.1) $3x10^{-2}$ Ωm. The observed shifts in elasticity and resistivity are shown to be induced by the associated changes in chemical bonding from van der Waals type in $BO_{1.5}$ to icosahedral type in the BOY phase.

More information can be found in: D. Music, V. Chirita, J.M. Schneider and U. Helmersson: Effect of chemical on the elastic properties of the boron-oxygen-yttrium system studied by ab initio and experimental means, *Physical Review B* 69, 092103 (2004).