

# High-Performance Ceramics

## Ceramics Processing on Atomic Scale by Control of Interface Parameter

W. Wunderlich



Wilfried Wunderlich graduated in Physics and received a Dr. rer. nat. degree in Chemistry from the Max-Planck-Institute for Metal Research, Stuttgart (Germany) in 1987. His research was honored by two scientific awards before he moved to Japan in 1996. He has been Associate Professor in the Intelligent Ceramics Processing group at the Nagoya Institute of Technology, Ceramics Research Laboratory Tajimi (Japan) since 2000.

### Abstract

This overview article describes observations at atomic scale on different ceramic interfaces and summarizes important interface parameters. In the past, the integration of ceramics into semiconductor devices has been mainly considered for the thin film deposition on a substrate. These epitaxial interfaces have indeed high strength due to an ordered arrangement of atomic bonds, but the mismatch between both crystalline lattices leads to the formation of misfit dislocations. They can leave the interface and destroy the good electric properties of the thin film. Buffer layers can avoid misfit dislocations at the interface. Three types can be classified as buffer layers reducing the misfit, the stress at the interface, or the dislocation migration. In substrate

thin-film geometry, the microstructure is determined by the ratio between surface and interface energy and can be manipulated. The trend of recent development, however, proceeds towards new processing methods like the deposition of nanoparticles or the wet chemical hydrolysis reaction. As these solid-gaseous or solid-liquid interfaces have higher reaction kinetics and mobility, the variety of engineering possibilities increases. In addition to segregation and monolayer deposition, polarization, adhesion, and surface coating of particles with inorganic molecules or polymers are now important phenomena. In all cases, the chemical bonding at the interface affects the materials properties, a knowledge of which is essential.

**KEYWORDS:** ceramics integration, interface properties, misfit dislocations, interface mobility, nanocomposites

InterCeram 51 (2002) 3

## 1 Introduction

Interfaces between ceramics and metals have a long history. Ancient artists produced gold decoration on sapphire or enamel ceramic layers on steel. Ceramic interfaces or grain boundaries are also model materials for the physicist, since the different bonding in the bulk crystal leads to special properties [1–4].

By understanding the chemical bonding across the interface, it is possible to manufacture interfaces with better properties. As in any crystal, also regarding interfaces, the knowledge about structure and physical properties is essential for the development and optimization of advanced materials. Especially the flow across the interface such as flow of atoms, heat, dislocations, or electric current can be influenced by the interface structure which offers the material science engineer many new possibilities.

For electronic devices, the epitaxial thin-film deposition has been mostly considered in the past, however, the current trend is towards wet-chemical processing [5, 6] and nanomaterials [7]. This paper cannot give a full description but can show concepts and directions in which conducting new research is worthwhile.

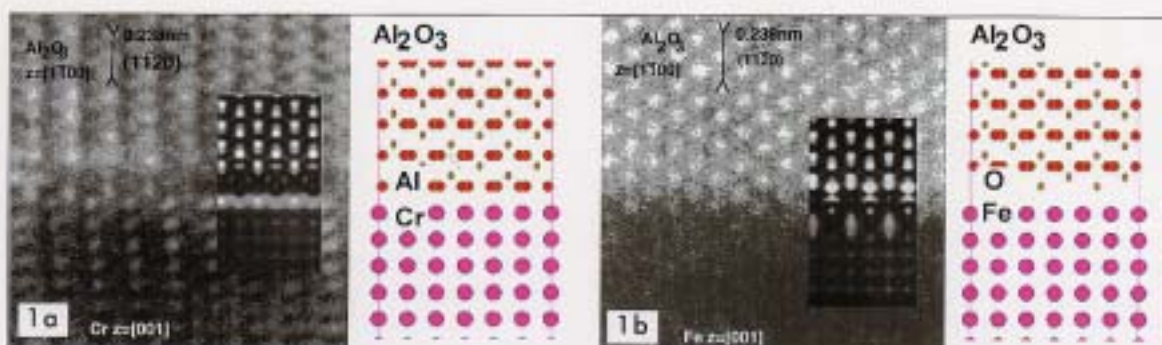
This paper concerns three general topics. First, how the chemical nature of bonding at the interface controls the interface properties like interface energy, strength, mobility and diffusivity. Second, structural aspects are discussed, especially the development of misfit dislocations at epitaxial interfaces. Third, the enormous possibilities of interface improvement by wet-chemical engineering methods are outlined and summarized.

## 2 Experimental Observations of Ceramic-Bonded Interface Structures

### 2.1 Atomic Bonding at Heterogeneous Interfaces: the Cr/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> Interface

The type of bonding across heterogeneous interface is the essential key point for understanding the interface properties. Similar to that of ceramic grain boundaries [1–4], the atomic bonds across the metal-ceramic interfaces influence the electronic band structure and hence all the interface properties. The first example (Figs. 1 a–b) shows the atomic structure of two metal-ceramic interfaces:

Figs. 1 a–b HRTEM micrograph with fitted image simulation and the atomic structure of:  
a) alumina-chromium interface;  
b) alumina-iron interface



- Cr- and Al<sub>2</sub>O<sub>3</sub>
- Fe- and Al<sub>2</sub>O<sub>3</sub>.

The interfaces are observed at the metallic particles embedded in the ceramic matrix. The specimens were produced by internal reduction, a special solid-state reaction, where the oxygen vapour pressure of a binary ceramic alloy, in this case Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>, was lowered [8]. The solid solution of the matrix separates into metallic particles inside the ceramic matrix according to the phase diagram.

The separation starts at the surface of the specimens where the reducing atmosphere removes the oxygen atoms. The metallic particles appear behind the migrating reaction front. The size can be adjusted according to the annealing time. The application for these alloys is, for example, as ceramic cutting tools where the soft metal particles lead to lubrication and enhance the wear resistance and, hence, the durability.

The formed particles are of hexagonal prismatic shape and show fixed orientation relationship between particle and matrix [8]. Figs. 1 a-b show the detailed analysis by High Resolution Transmission Electron Microscopy (HRTEM) for two different alloys, Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>. The insets show HRTEM image calculations, which are necessary in order to detect the exact atomic positions relative to the interface. The results show a significant difference for both alloys.

In the case of Al<sub>2</sub>O<sub>3</sub>-Cr, the interface has a dark contrast line on the ceramic side and a bright line at the metal side under the focus conditions for optimal resolution. In the case of Al<sub>2</sub>O<sub>3</sub>-Fe, it is the opposite. This phenomenon was observed for two zone axes; Figs. 1 a-b show only one of them, i.e.  $z = [001]$ . The atomic structure can be deduced from the simulated images. The results of this study are that, in the case of chromium, the metal atoms (Cr) are bonded to the aluminium atoms (Cr-Al bonding, Fig. 1a).

In the case of iron it is the opposite; the iron atoms bond to oxygen atoms of alumina (Fe-O bonding, Fig. 1b). This result shows that the atomic bonding at the interface depends on the material chemical constitution. Experience has shown that the type of bonding at the interface usually cannot be controlled physically, but only chemically by adding other chemical elements.

## 2.2 Heterogeneous Interface without Misfit Dislocations: AlN/TiN/MgO Interface

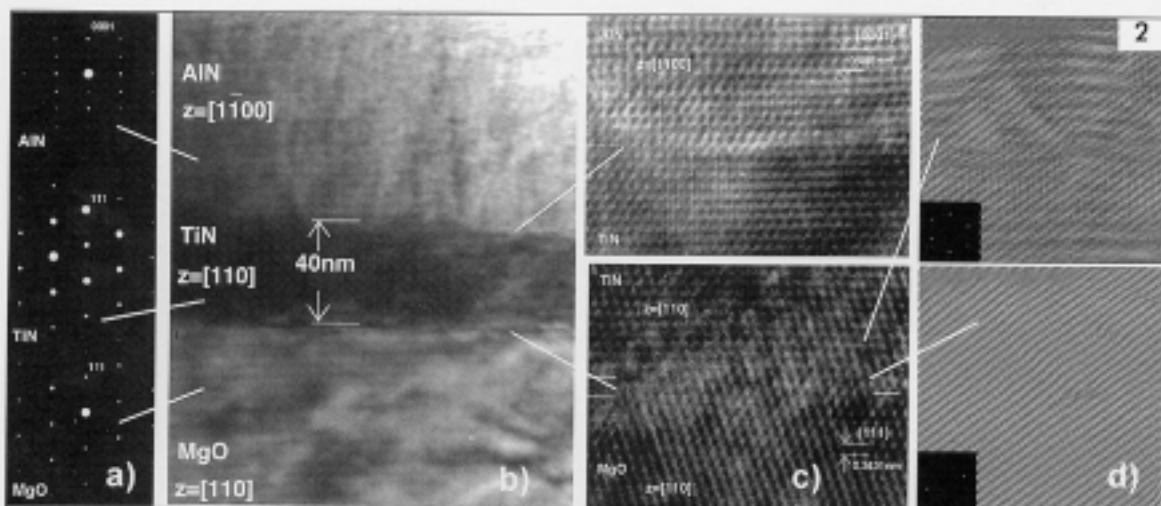
The following three examples show interfaces with high coherency which are required for functional electro-ceramics in thin-film technology. AlN or GaN thin films are important materials for blue laser diodes. For deposition of AlN on a MgO substrate, an intermediate buffer layer of TiN is grown (Figs. 2 a-d) [9] in order to reduce the mismatch between the MgO and AlN lattice constants.

The orientation relationship  $(111)_{AlN} // (001)_{TiN} <110>_{AlN} // <11.0>_{TiN}$  deduced from the diffraction pattern (Fig. 2a) follows the principle that closed packed planes and directions are parallel, which is very common between cubic and hexagonal lattices. In lower magnification (Fig. 2b), the three phases can be distinguished by absorption contrast due to the mass difference. The HRTEM-micrograph (Fig. 2c) shows the perfect coherency at both interfaces (AlN/TiN and TiN/MgO).

Since TiN has the same crystal structure as MgO, this interface is hard to detect in the HRTEM-micrograph (Fig. 2c). In order to analyse the interface in detail, the technique of image filtering is applied (Fig. 2d): the digitalized image is transformed to reciprocal space in the computer. Apertures are then set around the diffraction spots resulting from the lattice planes, and finally the image is transformed back to real space. This image processing is useful for detecting whether a misfit dislocation is present. Except for a single dislocation on the right side of Fig. 2d, this interface is perfectly coherent, showing the good performance of the buffer-layer concept.

## 2.3 Heterogeneous Interface with Misfit Dislocations: BaTiO<sub>3</sub>/SrTiO<sub>3</sub> Interface

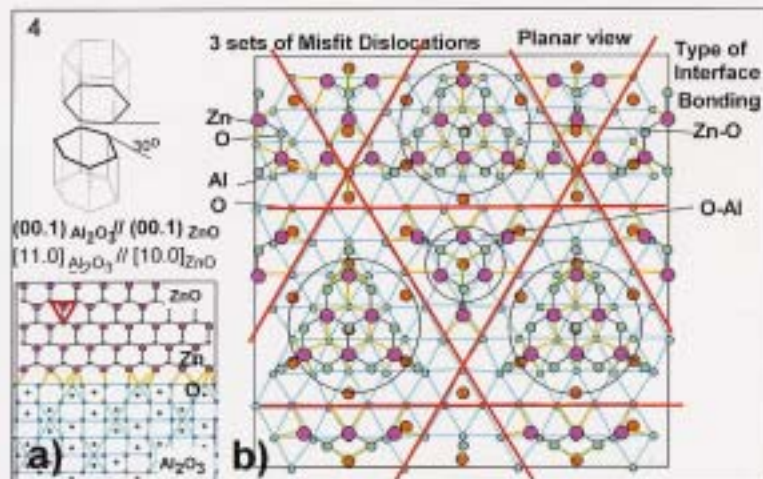
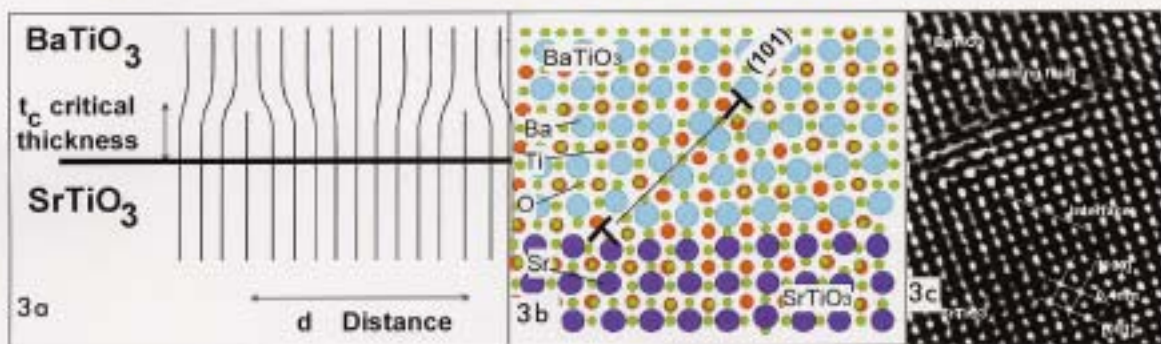
The interfaces become more complex if the difference in the lattice constants increases. The next example shows a semicoherent interface, namely between a SrTiO<sub>3</sub> substrate and a BaTiO<sub>3</sub> thin film (Figs. 3 a-c) [10]. Both materials have the same crystal type, i.e. perovskite, but with a misfit in the lattice constants. Below a certain thickness, the lattice of the thin film is strained and has the same lattice as the substrate. Above a certain thickness, the thin film introduces misfit dislocations to accommodate the misfit (Fig. 3a). In recently applied new processing



Figs. 2 a-d Interfaces between an AlN thin film on MgO substrate with a TiN buffer layer: a) diffraction spots; b) low magnification of TEM micrograph; c) HRTEM micrograph; d) filtering of the computerized image



**Figs. 3 a-c**  
The  $\text{BaTiO}_3/\text{SrTiO}_3$  interface:  
a) critical thickness for epitaxial growth;  
b) MD calculations of the stacking fault formation;  
c) HRTEM micrograph of the stacking fault



**Figs. 4 a-b**  
The  $\text{ZnO}-\text{Al}_2\text{O}_3$  interface:  
a) orientation relationship and cross-section;  
b) misfit dislocation network in planar view

techniques for thin-film growth, like Molecular Beam Epitaxy (MBE) or Plasma Laser Deposition (PLD), the process temperature can be decreased from 1400 to 700 °C and production becomes more efficient. However, due to the low temperature, the defects cannot annihilate and the thin film ultimately contains a lot of defects like misfit dislocations and stacking faults. In the TEM micrograph of the heterogeneous interface, the misfit dislocations are present.

The value of the critical thickness for epitaxial growth was calculated by Molecular Dynamics (MD) simulation [10]. The value is about four monolayers, which is about the interaction distance for electron wave functions across any interface or at surfaces. Furthermore, the formation mechanism of the stacking fault could be clarified (Fig. 3b). The misfit dislocation dissociates into two partial dislocations and one of them migrates to the interface. In between them the stacking fault is formed and the interface energy is reduced because two defects are combined. The atomic structure is identical to that deduced from the experimental HRTEM micrographs (Fig. 3c).

## 2.4 Heterogeneous Interface with Misfit Dislocation Array: $\text{ZnO}/\text{Al}_2\text{O}_3$ Interface

Interfaces can still be grown epitaxially if the two lattices at the interface consist of different crystal types, however, they then become more complex. The semiconducting wurtzite-type thin films, AlN, GaN, and ZnO, have excellent electronic properties with a wide band gap which is used for applications as blue laser diode. The goal of this process is to produce thin films without dislocations. On a basal (00.1) sapphire substrate the AlN thin film with wurtzite type structure was grown by CVD technique. The interface was analysed experimentally by X-ray analysis [11].

At the interface the c-axis of the two different hexagonal lattices are parallel, the a-axis are rotated by 30°.

The results for this interface are transferable to other thin films with wurtzite structure such as ZnO. Detailed analysis by MD-simulations (Fig. 4a) showed that the ratio of matching lattice planes is 8 : 9 in the case of the [1.00] AlN/[1-1.0]  $\text{Al}_2\text{O}_3$  interface whereas in the other cases,  $\text{ZnO}/\text{Al}_2\text{O}_3$  and  $\text{GaN}/\text{Al}_2\text{O}_3$ , the ratio is 5 : 6. Detailed analysis showed that, on atomic scale, two structural units at the interface appears: one with an atomic configuration like in ZnO with Zn-O bonds across the interface, the other similar to  $\text{Al}_2\text{O}_3$  with O-Al bonds. These findings lead to the interface model which is shown in the planar view (Fig. 4b). Between the bonded areas with the two types of structural units, misfit dislocations in three directions in periodical distances are present.

Although the geometry of this interface is complicated, it still has a semicoherent structure. Experience shows that coherency is observed for lattice mismatch up to 10–20 %, leading to misfit dislocations spacing of 2–20 nm. At epitaxial ceramic-ceramic interfaces, the spacing of the oxygen sublattice is usual regarded as relevant for the mismatch rather than the lattice constant itself, e.g. at the alumina-spinel interface [12].

## 3 Processing Concepts for Interfaces

### 3.1 Geometric Control

The conclusion from the aforementioned epitaxially grown interfaces is that a lot of effort is necessary to avoid the misfit dislocations. They result from the stress at the interface which is due to:

- the misfit between the lattice parameters
- the difference in thermal expansion coefficient
- bending stresses in the thin film
- nucleation at the surface of the thin film.

Experimental observations show that there are more dislocations lying at the interface than are usually needed for accommodating the misfit [10]. Hence, these dislocations are always a source of threading dislocations which leave the interface, migrate into the thin film, and destroy its good electric properties.

Several processing techniques for avoiding misfit dislocations have been considered (Figs. 5 a-d), and many patents have been published on this subject. When the substrate or the thin film is pre-stressed before or during the deposition, or at a heat treatment thereafter, the internal stress at the interface and hence the number of dislocations can be reduced (Fig. 5a). Usually straining the substrate parallel to the plane



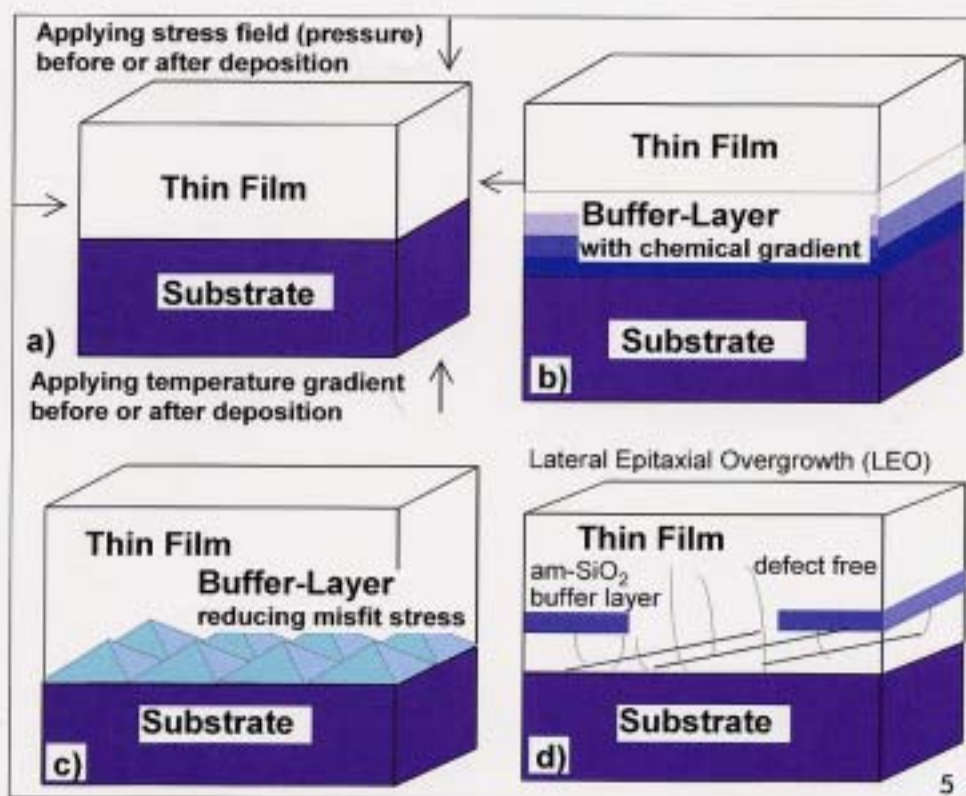
leads to a tensile stress at the interface which suppresses the dislocation nucleation. A compressive stress perpendicular to the substrate during cooling reduces the strain due to thermal contraction. Also by heat treatment, e.g. by moving a temperature gradient parallel or perpendicular to the thin film, the stresses at the interface can be released. An idea originating in metallurgy is to adjust the interface stress by using solid solution alloys for the thin film or substrate. In a ceramic alloy, the addition of foreign atoms with different ionic radii other than the host lattice changes its lattice parameters [13]. This effect can be used to adjust the lattice parameter at a heterogeneous interface.

The buffer-layer concept has been extended to the production of several buffer layers (Fig. 5b), leading to the so-called Functional Gradient Material (FGM) with a gradient in the chemical composition. These layers can either be produced by varying the composition during the sputtering process or by subsequent sintering of layers with different composition. The lattice mismatch or thermal mismatch is then divided into small parts at each interface. A new variant of the buffer-layer concept is the processing of faceted buffer layers (Fig. 5c). With the advanced MBE technique, the shaping of atomic layers in the required nanometer range is possible. The facets change the direction of the misfit stress usually occurring parallel to the interface into a component perpendicular to the interface. The inclined pyramidal facets re-direct the misfit stress and hence reduce the stress level at the interface itself. These faceted interfaces are also observed at naturally grown interfaces, especially when segregation occurs.

Finally, the idea shown in Fig. 5d considers the following: instead of avoiding the dislocation in the thin film their presence is accepted, only their spreading is stopped. With the so-called Lateral Epitaxial Overgrowth (LEO) [14] technique, a thin amorphous silica layer with periodical open spacings is grown which absorbs the dislocation stress. The subsequently deposited wurtzite thin film still grows epitaxially on the substrate and is dislocation-free when the LEO-technique is applied twice. Amorphous layers do not allow dislocations to penetrate as they act as barriers against dislocation movement.

### 3.2 Control of the Interface Energy

A physical knowledge of epitaxial interfaces is necessary for improving the properties of the thin films. The thin-film morphology is strongly influenced by the ratio of surface and interface energy of both materials as summarized in Fig. 6. This scheme is useful for designing the interface morphology by changing these energies. For each material composition, additions of third chemical elements change the interface or surface energy according to practical experience. This diagram (Fig. 6) can also be used in the opposite



way, namely to estimate the ratio of interface energies, when a certain morphology is observed. When on a substrate A with a certain surface energy  $\gamma_A$ , a material B is deposited with a surface energy  $\gamma_B$ , an interface with energy  $\gamma_{AB}$  is formed. The morphology of the composite material AB is caused by the contact angle at the interface which depends on the ratio of the interface energies (Fig. 6) [4, 6]. If the thin film (B) does not cover the substrate (A), either the interface energy is high or the surface energy of material B is high. Wavy interfaces or surfaces can occur when their energy is low, but since they are still in a metastable state, roughness can disappear if the system has enough time to relax the energy by subsequent heat treatment or if the growth is slow enough. The most suitable way to control the interface energy experimentally is by segregation of monolayers of other chemical elements. The phenomenon of segregation leads to amorphous grain boundary films in SiN-ceramics [4], however, it is still not yet completely understood.

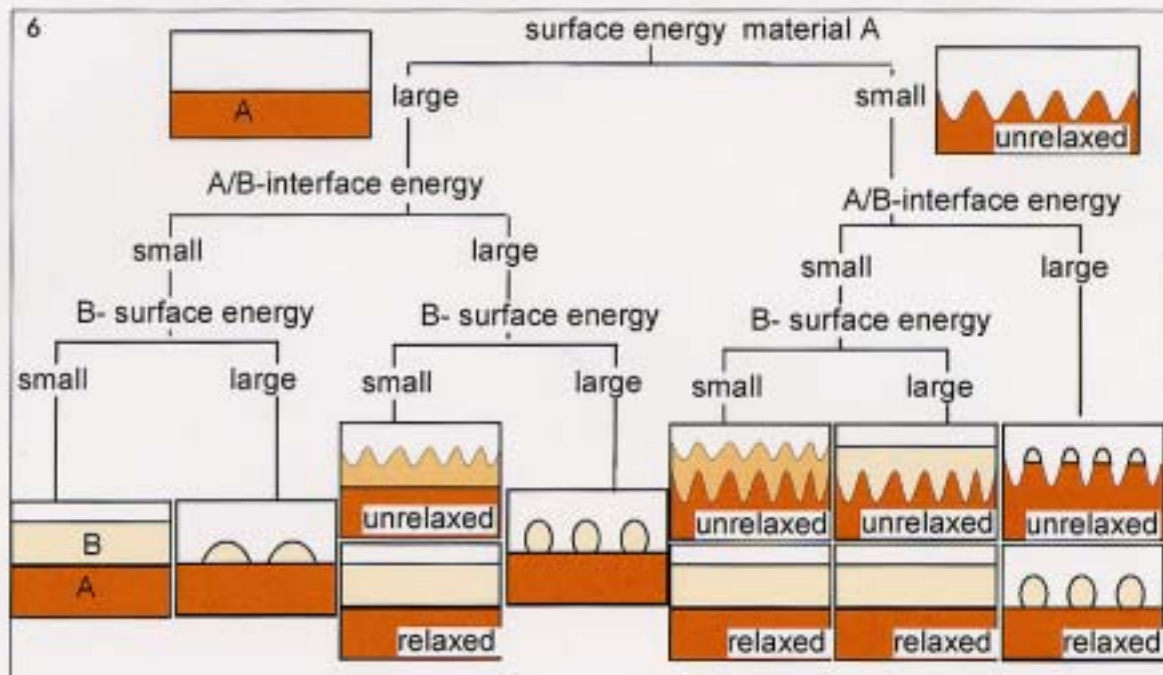
### 3.3 Migrating Interfaces at Solid-Solid Reactions

The above considerations about the interface morphology assumed that the driving force for interface migration is the reduction in interface energy. This physical force is in the order of 1–10 MPa, however, the chemical forces are in the order of >100 MPa. These occur when new thermodynamically stable phases are formed by solid-state reactions or transformations. The velocity of a migrating interface is given by the product of the driving force and the mobility of the interface. The mobility of the interface is thermally activated and the activation energy depends on the material composition and the orientation relationship between both crystals. Experimental results on grain boundaries, which can be transferred to interfaces as well, showed that this kinetic activation energy has no relation to the static structural energy

**Figs. 5 a–d** Processing concepts for avoiding misfit dislocation in thin-film substrates for electronic devices: a) remove the interface stress by applying pressure or a temperature gradient parallel or perpendicular to the substrate; b) in FGM a chemical gradient reduces the misfit stress; c) artificial facets processed by nanotechnology lead to a smooth stress gradient near the interface; d) amorphous buffer layers stop the spreading of threading dislocations from the interface into the thin film



Fig. 6  
The morphology of a substrate A and a thereon-deposited thin-film B depends on the interface and surface energies of each phase



usually referred to as interface energy and hence, four cases can be distinguished [15]: interfaces with low or high structural energy, and/or interfaces with low or high kinetic energy. For each interface these two independent energies have to be considered and controlled.

During physical transformation, the heat is transferred through the interface and in a chemical reaction, the atoms have to additionally penetrate through the interface between the two materials. The flow of heat or atoms depends on the permeability of the interface; a parameter, which depends on the material composition. Some interfaces are diffusion barriers, others are heat barriers, at which even after a long time no atom or heat exchange occurs. Both types of interfaces act independently. Research on the thermal coating of turbine blades shows that  $ZrO_2$  is a good thermal barrier material; Ir-Al, Ir-Si alloys are oxygen diffusion barriers; and  $Si_3N_4$  is a corrosion barrier.

All coatings are necessary for optimal performance of high-temperature turbine blades. Independent of permeability is the driving force for the heat transfer or the atom transfer. These driving forces depend on the heat gradient or the concentration gradient in front of the migrating interface. These gradients depend on the heat conductivity, diffusivity, and solubility of foreign atoms in each phase. Numerical simulations are necessary for studying these processes.

The above-mentioned phenomena were considered for the thin-film geometry, however, they can be easily transferred to the spherical particle geometry in a chemical reactor [6]. In a chemical reaction, the reactant and the reaction product penetrate into the particle or exit it in the same direction, namely from the surface. The progress in time of such a chemical reaction depends on three main factors: the diffusion of the reactant to the reaction front, the chemical reaction itself, or the diffusion of the reaction products away from the interface, which is often related to the migration of the reaction interface. In the case of powder geometry, the relation of these

three constants depending on time leads to the two following reaction types:

- the shrinking sphere model is obtained when no diffusion barrier for removing the reaction products occurs either due to high permeability, flaking, peeling of the reaction product or when gaseous reaction products are formed.
- The shrinking core model occurs when the reactant has a slow diffusivity towards the reaction front. This can lead to incomplete reactions and often a core-shell structure occurs inside the particles.

#### 4 Parameter Control during Processing

##### 4.1 Nanotechnology

When the particle radius reaches nanometer dimensions, special size-effects occur such as surface relaxation of the particles, or thicker grain boundary regions, compared to usual polycrystalline materials [16]. The atoms in these regions are weakly bond compared to standard polycrystals and hence, nanosized materials show special properties. Processing techniques for nanomaterials are sputtering, crushing, ball-milling, ion bombardment, fast crystallization from amorphous material or liquids, condensation of vapours, but the most effective one is by chemical reaction, e.g. during the sol-gel process. After washing and drying, the nanopowder can be sintered into a nanocrystalline material with grain sizes  $< 10$  nm, when the grain growth can be suppressed. The small size allows the production of composite materials of usually immiscible phases with fast inter-diffusion [17]. The nanocomposite microstructure can be classified in intra-, inter- or nano-nano-composite materials regardless the nanoparticles are surrounded by or lie in between other grains, or are equal in size [7]. An example for ceramics integration are nanosized metal particles with their special magnetic coercivity such as Fe or Co, which have to be covered by an oxide layer in order to protect the grain growth and chemical reactions [18]. The formation of the oxide layer can be achieved by changing the oxygen partial pressure in the reaction chamber.



## 4.2 Particle Interactions in the Slurry

Conventional ceramics processing is mainly based on slurries [5–7] in which the raw materials are present in aqueous solution. Chemical reactions in the slurry are liquid-solid or gaseous-solid reactions and are much faster than solid-solid ones with a larger variety of possibilities. Besides the crystalline ceramic raw materials, the slurry also contains surfactants, catalysts, enzymes, ions, electro-conducting polymers or insulating polymers, and other molecules. In rheology, these interaction forces occurring in the slurry between the particles and molecules are classified (Fig. 7), for example, as Coulomb, polarization, Van-der-Waals, steric, capillarity, adhesion and hydrophilic forces. The Discrete Element Method (DEM) [19] tries to find a numerical description for these forces. The electrostatic forces are expressed by the so-called zeta potential curve which strongly depends on the pH value. It is zero at the isoelectric point where the repulsive and attractive forces are in balance. Under these conditions, the molecules try to arrange themselves in the densely packed manner and often the liquid gel transform to a solid-like sol. The polarisability of the particles is the important parameter in these solutions as well as the time constant for relaxing an excited electronic state. Since the number of parameters is larger, the interface engineer has more possibilities. The goal of ceramics processing is to adjust the forces between the particles so that they not only bond together, but also repel each other, finally resulting in the formation of a colloidal crystal.

## 4.3 Self-Organization of Titania Precursor Molecules on Si Substrate

Organic molecules suitable for ceramic processing are those with reactive groups, for example, sebacic acid with its two acid groups could be successfully used for aqueous processing of AlN [20]. The second requirement for advanced ceramics processing is the self-organization of the polymer molecules, which means the ordering of molecule chains, e.g. by weak Van-der-Waals forces. This phenomenon

can be used to produce Self-Assembled Monolayers (SAM), which means monolayers that are ordered by molecular forces. These organic molecules can have two functions:

- They are templates for further bonding or structuring the ceramic particles, either on a flat substrate or on a round particle for keeping the distance between the particles.
- They are directly used as precursors, which means they get oxidized during burning, the carbon chains are removed, and the material transforms to the inorganic ceramic.

One example for the successful use of this self-assembling technique is the production of titania monolayers on Si-substrates shown schematically in Fig. 8 [21]. The first step is the deposition of the organic monolayer. On a (100) Si-substrate the organic molecule (in this example octadecyltrichloro-silane OTS or 3-amino-propyl-tri-ethoxy-silan (APTS),  $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$  or phenyl-tri-chloro-silane PTCS) is deposited by immersing the substrate into its toluene anhydrous solution. The hydrolysis reaction occurs under nitrogen atmosphere during which the Si atoms are bonded to the substrate. The surface of this organic self-assembled monolayer consists of methyl and octadecyl groups, or in the case of N-containing molecules, of phenyl groups.

This organic-anorganic composite can now be, in the second step, irradiated with UV-light and after 2 h the irradiated regions become hydrophilic due to Si-OH group formation, while the non-irradiated regions remain unchanged, which means the hydrophobic octadecyl- or phenyl- groups remain. The third step is the deposition of a ceramics precursor material, e.g. titanium-dichloride-di-ethoxide (TDD). Under the release of water molecules, bonds between the  $(\text{Ti}(\text{OC}_2\text{H}_5)_2(\text{OH})_2)$  complex and the substrate form (bond formation). Then the substrate is fired at temperatures  $< 120^\circ\text{C}$  to remove the residual solvents and to promote the chemisorption of the Ti-complex with the silan-monolayer on the substrate.

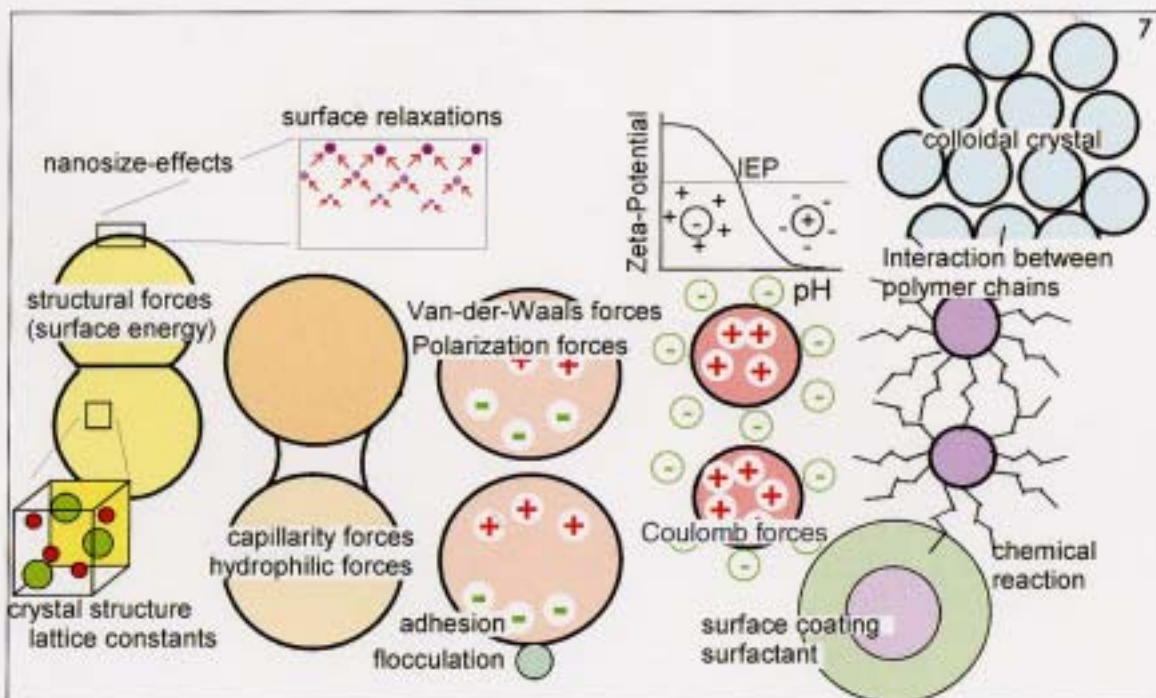
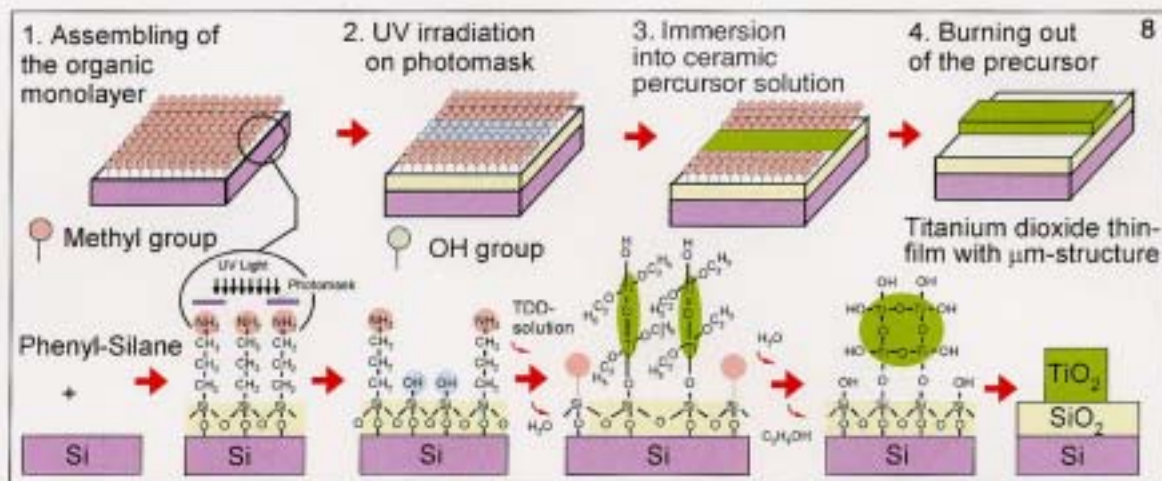


Fig. 7 Interaction effects in the aqueous slurry used for ceramic processing



**Fig. 8**  
Process steps for manufacturing structured  $\text{TiO}_2$  thin films on Si-substrates by self-assembled organic monolayers



The last step is the burn-out of the polymer molecules so that finally the inorganic ceramic remains. With this process it is possible to produce a micropattern of anatase-based ceramics with dimensions in the micrometer range [21].

#### 4.4 Interface between Organic Molecules and Ceramics: Phtalocyanine Metal on ZnO

The interfaces between polymer molecules and ceramics are more complicated than epitaxial interfaces as the symmetry is low and the rotation molecules can occur. The example (Figs. 9 a–e) shows the bonding between the organo-metallic macromolecule phtalocyanine metal (PcM) and the ZnO (001) surface.

The PcM molecule consists of one metallic atom in the middle, e.g. Co, Fe, or Ti surrounded by nitrogen atoms, pyrrol and benzol rings, four each. The advantage of these polymers is their electric conductivity and the excitation of an electronic band by visible light. Hence, the application of this material has become important as photoreceptor devices in laser beam printers and recently also as possible candidate for dyes in advanced solar cells [22].

For this purpose, the PcM macromolecules are bond onto ZnO substrates and at their interface the excited electrons can jump into the highest ZnO orbital and be removed by the applied voltage.

At the interface four possible geometries by the bonding process (Fig. 9c) between the macromolecule and the ZnO (001) surface can occur whether it is the tip (Fig. 9b), the edge (Fig. 9c), the small side (Fig. 9d), or the base side (Fig. 9e) of the macromolecule bonds to ZnO. The selection realized in these cases can be achieved by adapting reactive molecular groups such as  $\text{SO}_x$  on the edges of the macromolecule. Depending on the amount of these bonding aids, one of the four cases occurs. The preparation, separation, and even the characterization of the polymer molecule orientation are still challenges to be faced, however, self-organized layers can be grown [23].

#### 5 Summary and Outlook

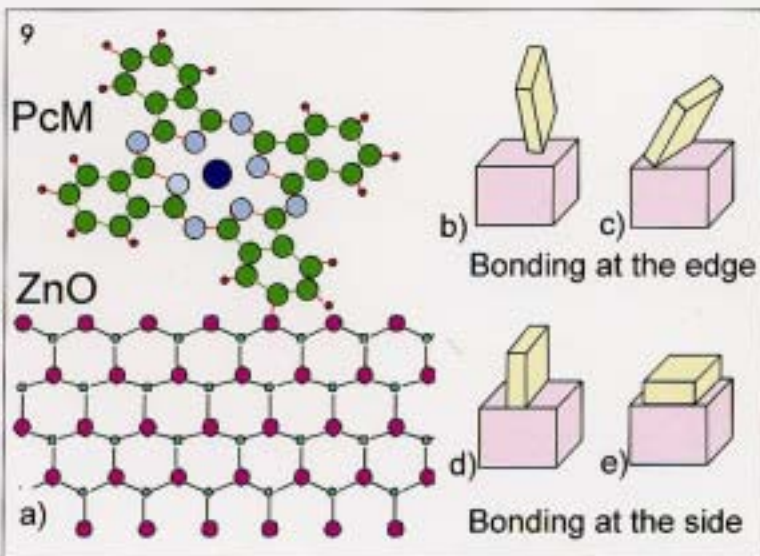
The experimental observations of ceramic interfaces showed that the control of atomic bonds across the interface is the key point for improving ceramic integration in electronic devices or other applications. The goal of interface engineering is the improvement of chemical bonding across the interface. Modern MBE, PLD or CVD deposition techniques allow the growth of monolayers with defined dimension in vertical and horizontal direction and it becomes possible to develop gradient layers, artificial lattices, super-lattices or non-stoichiometric layers.

Systematic studies about the influence of segregation elements are necessary for improving the bond strength between ceramics and other materials directly or indirectly by controlling the interface properties, like permeability and reactivity.

Epitaxial ceramic thin films, however, are sensitive against thermal or mechanical stress, so the recent trend of processing proceeds towards soft materials produced with nanotechnology or wet-chemical methods. The variety of experimental parameters and processing possibilities at solid-liquid and solid-gaseous interfaces are wider than for solid-solid interfaces.

With clearly defined demands from the developers of new devices, the interface engineer can direct more efforts towards processing and optimizing these interfaces.

**Figs. 9 a–e**  
PcM–ZnO interface:  
a) atomic model;  
b–e) structural models with increasing degree of bonding between the macromolecule (PcM) and the inorganic surface (ZnO)





## References

- [1] D. Wolf, S. Yip: *Material Interfaces*, London: Chapman & Hall, 1992
- [2] A.P. Sutton, R.W. Balluffi: *Interfaces in Crystalline Materials*, Oxford: Clarendon Press, 1995
- [3] W. Wunderlich: Symmetrical Tilt Grain Boundaries in Zinc Oxide. *Phys. Stat. Sol. (a)* 170 (1998) 99-111
- [4] I. Tanaka: Intergranular Glassy Films in Ceramics. *J. Cer. Soc. Japan* 109 [8] (2001) 127-134
- [5] J.A. Lewis: Colloidal Processing of Ceramics. *J. Amer. Ceram. Soc.* 83 (2000) 2341-59
- [6] T.A. Ring: *Fundamentals of Ceramics Processing and Synthesis*. San Diego: Academic Press, 1996
- [7] K. Niihara: New Design Concept of Structural Ceramics - Ceramic Nanocomposites. *J. Cer. Soc. Japan (Seramikusu Ronbunshi)* 99 [10] (1991) 974-982
- [8] M. Beckhaus-Ricault, S. Hagege, A. Peyrat, P. Moreau: Internal Reduction of Chromium-doped alumina. *J. Amer. Ceram. Soc.* 77 (1994) 423-430
- [9] N. Shibata, S. Okubo, Y. Saito, W. Wunderlich, Y. Ikuhara: Formation of Cubic-AlN Layer on MgO (100) Substrate by Ion-Assisted MBE. *Proc. 7th Int. Conf. on Nitride Semiconductors ISCN'1997 Tokushima*, Ed. Isamu Akasaki, et al. *Jpn. Soc. Appl. Phys.* (1997) 374-375
- [10] W. Wunderlich, M. Fujimoto, H. Ohsato: Molecular Dynamics Simulation about Misfit Dislocations at the BaTiO<sub>3</sub>/SiTiO<sub>3</sub> Interface. *Thin Solid Films* 375 (2000) 9-14
- [11] H. Ohsato, T. Kato, S. Kaketsu, R. D. Saxena, T. Okuda: X-Ray Analysis of the Alumina/GaN Interface. *J. Cryst. Growth* 189/190 (1998) 202
- [12] D. Hesse, S. Senz, R. Scholz, P. Werner, J. Heydenreich: Structure and Morphology of the Reaction Fronts during the MgAl<sub>2</sub>O<sub>4</sub> Thin Films. *Interface Science* 2 (1994) 221-226
- [13] H. Ohsato, J. Sugino, A. Komura, S. Nishigaki, T. Okuda: Microwave Dielectric Properties of Ba<sub>1-x</sub>(Nd<sub>1-y</sub>R<sub>y</sub>)Ti<sub>1-y</sub>O<sub>3</sub> (R = Eu, Dy, Ho, Er and Yb) Solid Solution. *Jpn. J. Appl. Phys.* 38 [9] (1999) 5625-5628
- [14] M. Razeghi: MOCVD technology and its Application. In: *Handbook on Semiconductors*, Vol. 3. Ed. T.S. Moors. Elsevier Publ. (1994) p.183
- [15] W. Wunderlich: Theoretical Considerations about Grain Boundary Migration in fcc Metals. *Mat. Sci. Forum* 207 (1996) 141-144
- [16] W. Wunderlich, Y. Ishida, R. Maurer: HRTEM-observations of Nanocrystalline Palladium. *Scripta Met.* 24 (1990) 403-404
- [17] K. Pixius, W. Wunderlich, J. Schütz, W. Amend, H. J. Meyer: A Microscopic Model for the Mechanical Alloying of Silicon and Germanium. *Scripta Met. Mat.* 33 (1995) 407-413
- [18] D. J. Peng, K. Sumiyama, S. Yamamoto, T. Hihara, T. J. Kanno: Magnetic Properties of Mono-dispersed Co/CoO Clusters. *Phys. Review B* 61 (2000) 3103-3109
- [19] Chu-Wan Hong: New Concept for Simulating Particle Packing in Colloidal Forming Process. *J. Amer. Ceram. Soc.* 80 (1997) 2517-24
- [20] Y. Kataoka, S. Chang, M. Oya, M. Takahashi: Aqueous Processing of Aluminum-Nitride Using Sebacic Acid. *Proc. Japanese Ceramics Society Annual Autumn Meeting 2000*, 2F09 148
- [21] Y. Masuda, T. Sugiyama, H. Lin, W. S. Seo, K. Koumoto: Selective Deposition and Micropatterning of Titanium Dioxide Thin Film on Self-assembled Monolayers. *Thin Solid Films* 382 (2001) 153-157
- [22] T. Yoshida, M. Tachimoto, D. Schlettwein, D. Währle, T. Sugiura, H. Minoura: Self-assembly of Zinc Oxide Thin Films Modified with Tetrasulfonated Metallaphthalocyanines by One-Step Electrodeposition. *Chemistry of Materials* 11 [10] (1999) 2657-2667
- [23] D. Schlettwein, H. Tada, S. Mashiko: Substrate-Induced Order and Multilayer Epitaxial Growth of Substituted Phthalocyanine Thin Films. *Langmuir* 16 (2000) 2872-2881

Received: 12.02.2002  
Accepted: 18.02.2002

### Wilfried Wunderlich Nagoya Institute of Technology

Ceramics Research Laboratory, 507-0071 Tajimi, Japan, e-mail: wi-wunder@rocketmail.com

## Kurzfassung / Résumé / Resumen

### Keramik-Herstellung auf atomarer Ebene durch Kontrolle der Grenzflächen-Parameter

Dieser Übersichtsartikel beschreibt Untersuchungen auf atomarer Ebene an verschiedenen Keramik-Grenzflächen und fasst wichtige Grenzflächen-Parameter zusammen. In der Vergangenheit wurde versucht, Keramikwerkstoffe durch das Abscheiden von Dünnschichtfilmen in Halbleiter-Bauelemente zu integrieren. Diese zumeist epitaktischen Grenzflächen haben eine hohe Festigkeit durch die geordneten Atombindungen an der Grenzfläche, aber eine Fehlpassung der Gitterkonstanten führt zur Ausbildung von Grenzflächenversetzungen. Diese können die Grenzfläche verlassen und die guten elektrischen Eigenschaften der Dünnschichtfilme verschlechtern. Pufferschichten können Misfit-Versetzungen unterdrücken und nach der Wirkungsweise in drei Arten klassifiziert werden, und zwar in Schichten, die den Misfit,

die Spannungen an der Grenzfläche oder die Ausbreitung der Versetzungen vermindern. Bei der Abscheidung von dünnen Filmen auf dem Substrat hängt die Mikrostruktur von dem Verhältnis von Oberflächenenergie zu Grenzflächenenergie ab und kann gezielt manipuliert werden. Der Trend der derzeitigen Entwicklung geht jedoch in Richtung neuer Herstellungsmethoden, wie die Abscheidung von Nano-Teilchen oder nasschemischer Reaktionen. Diese fest-flüssigen oder fest-gasförmigen Grenzflächen weisen eine höhere Reaktionskinetik und Beweglichkeit auf und die Möglichkeiten für die Prozessführung nehmen zu. Zusätzlich zu Segregation und Ausbildung von Pufferschichten treten nun Polarisation, Adhäsion, Oberflächen-Coating von Teilchen mit anorganischen Molekülen oder Polymeren als wichtige Phänomene auf. In allen Fällen beeinflusst die chemische Bindung an der Grenzfläche diese Werkstoffeigenschaften, und deren Verständnis ist für die Optimierung wichtig.

### Ingénierie des céramiques à l'échelle atomique, par contrôle des paramètres interfaciaux

Cet article de revue décrit les observations à l'échelle atomique sur différentes interfaces céramiques et récapitule les paramètres interfaciaux importants. Dans le passé, l'intégration des céramiques dans les systèmes semi-conducteurs a essentiellement concerné la déposition de couche mince

sur substrat. Ces interfaces d'épitaxie offrent une haute résistance mécanique grâce à l'arrangement ordonné des liaisons atomiques, mais la différence entre les deux réseaux cristallins conduit à la formation de dislocations de désaccord. Ces dislocations peuvent migrer depuis l'interface et altérer les bonnes propriétés électriques de la couche mince. Des couches tampons peuvent éviter les dislocations de désaccord à l'interface. On peut considérer trois types de couches



tampón, selon qu'elles réduisent le désaccord, ou la contrainte interfaciale, ou la migration des dislocations. Dans la géométrie substrat / couche mince, la microstructure est déterminée par le rapport entre les énergies de surface et d'interface, et peut donc être modifiée. Le sens des développements récents, cependant, est d'aller vers de nouveaux procédés, comme le dépôt de nano-particules ou la réaction d'hydrolyse chimique en voie humide. Comme les interfaces solide-gaz et solide-liquide ont des valeurs accrues de

cinétique de réaction et de mobilité, on accroît les possibilités d'ingénierie. Outre la ségrégation et le dépôt de monocouches, les nouveaux phénomènes importants sont la polarisation, l'adhésion, et le revêtement de la surface des particules par des molécules inorganiques ou des polymères. Dans tous les cas, les propriétés des matériaux sont affectées par la liaison chimique à l'interface, dont la connaissance est essentielle.

---

#### **Procesamiento de materiales cerámicos a escala atómica a través del control de los parámetros interfaciales**

Este resumen describe investigaciones a escala atómica sobre diferentes superficies cerámicas y resume importantes parámetros interfaciales. En el pasado, la integración de materiales cerámicos en componentes semiconductores fue realizada por medio del depósito de capas finas. Estas capas generalmente epitaxiales presentan una alta resistencia debido a las valencias atómicas ordenadas en la superficie, pero diferencias en las constantes cristalinas conducen a dislocaciones interfaciales, que pueden abandonar la interfase, deteriorando las propiedades eléctricas de la capa. Capas intermedias pueden reducir estas dislocaciones. Según el modo de actuar, estas capas se pueden clasificar en tres tipos: capas que reducen la mala adaptación, las tensiones

en la interfase o la propagación de las dislocaciones. En la geometría de las micro-capas, la microestructura está determinada por la relación entre la energía superficial y la energía interfacial, que puede ser manipulada adecuadamente. Los nuevos procedimientos, sin embargo, están basados en el depósito de nanopartículas o la reacción hidrolítica en húmeda. Debido a que estas interfases sólida/gaseosas o sólida/líquidas tienen una más alta cinética de reacción y mayor movilidad, aumenta la variedad de posibilidades de actuar sobre el proceso. Conjuntamente con la segregación y el depósito de capas intermedias, ganan importancia otros fenómenos como polarización, adhesión y el revestimiento de partículas con moléculas inorgánicas o polímeros. En todos los casos, el enlace químico en la interfase tiene influencia sobre las propiedades del material, y el conocimiento de estas relaciones es esencial.