Montanuniversität Leoben

# Influence of Dopants in Oxide-based Coatings Deposited by Thermal CVD



Accomplished at the Department of Physical Metallurgy and Material Testing of the University of Leoben in cooperation with Materials Center Leoben

Leoben, June 2009

### Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Leoben, June 2009

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8 APPENDIX

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# 1 Introduction

Due to the increasing quality requirements and market competition, the metal cutting industry is forced to produce cutting tools which allow higher cutting speeds with simultaneous higher product life and process improvement for materials which are difficult to machine [1]. The outermost region of a cutting tool crucially influences chemical stability (corrosion, oxidation), wear resistance (abrasion, diffusion) and physical properties (e.g. thermal conductivity). Among other things, these qualities can be improved by depositing different coatings on the tool surface which include III-V and II-VI elements, borides, carbides, nitrides, oxides and sulphides [2]. The most common coating methods for cemented carbide cutting inserts are CVD (chemical vapor deposition) and PVD (physical vapor deposition) whereby particularly hard coatings of TiN, TiC, Ti(C,N) and Al<sub>2</sub>O<sub>3</sub> can be produced. For the selection of suitable deposition system, in order to achieve optimal coating properties, many different factors are important. Fig. 1.1 gives an overview of some main influences [2-4].



Fig. 1.1: Relationship of process parameters, CVD phenomena and coating properties [2].

The choice of the coating process is influenced by many factors such as substrate material, deposition temperature limits and application. This work deals with  $Al_2O_3$  based coatings deposited by CVD, hence this technology will be described in detail.

The development of protective coatings started during the 1950's, when TiC coatings on steel substrates were applied. The first commercial CVD TiC coatings were introduced in 1969. In 1970's the  $Al_2O_3$  coatings revolutionized the market [2]. A wide range of applications especially in the metal cutting and metal forming industry could be covered by developing TiC, Ti(C,N), TiN and  $Al_2O_3$  multilayer coatings. In 1980's PVD technology partly substituted the traditional CVD process, particularly for cutting applications where sharp edges and toughness are important. However, CVD is still the only coating system which allows the production of high quality  $Al_2O_3$  coatings on industrial scale [2, 3, 5].

This thesis focuses on CVD of Al<sub>2</sub>O<sub>3</sub> coatings without and with the addition of doping elements. Deposition experiments were carried out in order to optimize the coating process, especially for dopant precursors with melting and boiling temperatures different from standard temperature. The doping elements have been selected with regard to the improvement of the Al<sub>2</sub>O<sub>3</sub> coatings and thermodynamic calculations. The precursor melting and boiling temperature were important for the doping element selection, due to limitations of the laboratory scale deposition plant. Furthermore, the thermodynamic calculations and reported beneficial effects were considered. The aim of the thesis was to give information about the handling of the different precursor materials during the coating process and the influence of doping elements on coating properties. The chemical composition, phase formation, hardness and high temperature oxidation of the coatings was investigated. Finally, process parameters and guide lines for an upscailing of promising doping systems were identified.

# 2 Theoretical fundamentals

### 2.1 Chemical vapour deposition

CVD is a thermally activated process where chemical reactions cause the deposition of materials out of gaseous precursors. Different CVD methods have been developed in order to produce coatings which meet the requirements for several applications, like semiconductors and dielectrics for microelectronics or the deposition of wear resistant hard coatings which offer protection against oxidation or corrosion. The key benefit of CVD is its high throwing power which allows the deposition of uniform coatings on complex shaped components which may consist of conductive as well as non-conductive materials [2].

Independent of the specific process type, each CVD plant consists of three fundamental components:

- Chemical vapour precursor supply system
- CVD reactor
- Effluent gas handling

A typical CVD production system for cemented carbide indexable inserts is shown in Fig. 2.1. Supplied by gas bottles, the pure gases arrive the evaporator where the precursor materials will be vaporized and deposited on the substrates placed in the horizontal coating furnace. The exhaust (mainly HCI) will be neutralized in the gas purifier by NaOH and the waste  $H_2$  diluted below the explosive limit.



Fig. 2.1: Schematic of a CVD production unit [6].

#### 2.1.1 CVD processes

During the last decades, various CVD technologies for high-quality thin film production have been developed. In the early 1970ies, cutting industry started to deposit wear resistant hard coatings at high temperature ranging from 900 °C to 1100 °C (HT-CVD). Adaptation of the precursor system (e.g.  $C_2H_3N$ ) allows lower temperatures (750 – 900 °C, MT-CVD). A further reduction of the deposition temperature can be achieved by using metal organic precursors (~300 °C, MO-CVD) [2, 7]. An overview about the most important CVD processes is given in Tab. 2.1. Further CVD coating processes are flame assisted vapor deposition, electrochemical vapor deposition, atomic layer epitaxy, chemical vapor infiltration, laser enhanced CVD and plasma assisted CVD for temperature sensitive substrates. The thermally activated CVD processes can also be classified according to the deposition pressure: i) atmospheric pressure CVD, ii) low pressure CVD and iii) ultrahigh vacuum CVD [2, 3]. The HT-CVD process at atmospheric pressure is utilized within this thesis.

Method	HT-CVD	MT-CVD	PA-CVD	PVD		Diamond deposition
	TIN		TiN	TiN		pure diamond
Coatings	TIC	TON	TIAIN	TION	HAIN	
	HCN	HCN	HCN	HCN		
	Al <sub>2</sub> O <sub>3</sub>					
				Electron beam	Sputter	Hot filament
			Pulsed	ion plating; Arc	ion	microwaya
Processes		LP-CVD	plasma	ion plating;	plating;	nlasma:
			CVD	sputter ion	Arc ion	plasma,
				plating	plating	Plasma torch
T <sub>dep.</sub> [C°]	900-1100	750-900	600-900	300-600	300-600	700- 1000

Tab 2.1. Coating processes	and hard coatings	commonly used for	carbide cutting tools [3]
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Concerning the deposition conditions, there are three different regimes in a CVD process which are distinguished by the respective limiting reaction [2, 8].

- Thermodynamically controlled
- Surface kinetics or nucleation controlled
- Mass transport controlled

#### 2.1.2 Thermodynamics

The thermodynamics describe the conditions of systems according to their change in temperature, compression and volume and consequently provides information about the stability of these systems. In order to know whether the reaction takes place or not, the Gibbs free energy change  $\Delta G_r$  have to be calculated. The free-energy function G is defined according to Eq. 2.1 where H is the enthalpy, S the entropy, and T the absolute temperature [4].

$$G = H - TS$$
 2.1

In case of a constant temperature, the Gibbs free energy change  $\Delta G_r$  can be calculated by subtraction of the energy of formation for the product  $\Delta G_{f-product}$  and for the reactants  $\Delta G_{f-reactant}$  as shown in Eq. 2.2 [2, 4].

$$\Delta G_r = \Delta G_{\rm f-product} - \Delta G_{\rm f-reactant}$$
 2.2

The Gibbs free energy change  $\Delta G_r$  depends on the type of reactants, the molar ratio of these reactants, the process temperature and the process pressure. This dependency is presented in Eq. 2.3 and Eq. 2.4 [4].

$$\Delta G_r = \Delta G_{f^0} + RT * \ln Q \tag{2.3}$$

$$K = Q = \prod_{i} a_{i}^{z_{i}}$$

where R is the gas constant, T the temperature,  $\Delta G_{f^0}$  the standard free energy change of formation,  $\Pi_i a_i^{z_i}$  is the product of the activities of the species "i" in the reaction, and  $a_i$  is the stoichiometric coefficient of species "i" of the CVD reaction. Every system will naturally tend to minimize its free energy. The three cases below list the reaction behavior at a positive, a negative and an equal free energy change [4].

∆G <sub>r</sub> = 0	equilibrium,	no driving	force for	change
	• • • • • • • • • • • • • • • • • • •			•

- $\Delta G_r > 0$  no spontaneous reaction
- $\Delta G_r < 0$  spontaneous reaction

In the case of equilibrium which means  $\Delta G_r = 0$ , the free energy change can be calculated with Eq. 2.5 [4].

2.5

$$\Delta G_{c_0} = -RT * \ln K$$

where K is the equilibrium constant and follows from Eq.2.5:

$$K = \exp\left(\frac{-\Delta G_{f^0}}{RT}\right)$$
 2.6

Thermodynamic calculations and solutions are a useful tool for predicting promising deposition conditions. However, CVD is a non-equilibrium process and thermodynamic calculations can only provide basic information. A more precise prediction of a process feasibility can be achieved by considering the chemical kinetics and mass transport phenomena [2].

#### 2.1.3 Mass transport and kinetics

Mass transport, e.g. sufficient supply of reactants and desorbtion of by-products, makes a large contribution to deposition growth rate and coating thickness distribution [7]. There are two different phenomena, influencing the transport of gases from the reactor inlet to the specimen (Fig. 2.2) which have to be distinguished [2].

- Fluid dynamics, i.e. fluid flow, mass transfer and heat transfer of the reactants
- Mass transport of reactants close to the substrate surface



Fig. 2.2: Schematic illustration of the key steps in a CVD process: (1) Evaporation of precursors,
(2)+(3) mass transport, (3a) undesired homogeneous gas phase reaction, (4) heterogeneous reaction,
(5) diffusion process, (6)+(7) evacuation of by products and leaving the deposition chamber [2].

Gaseous precursors will be generated and transported into the reaction chamber (step 2-3). If the chemical reaction occurs within the reactor two places are possible, which can be "active" simultaneously [2].

- The undesired homogeneous gas phase reaction occurs at high temperature above the decomposition temperature of the intermediate species, displayed in step 3a.
- At temperatures below the dissociation of the intermediate phase, diffusion through the boundary layer (3b) and a following heterogeneous reaction takes place at the gas-solid interface, as can be seen in step 4. The deposited species diffuse along the heated substrate, crystallise and grow (step 5). The by-products and the non-reacted elements diffuse through the boundary layer and leave the deposition chamber (Step 6 and 7).

The boundary layer thickness can be estimated by calculating the dimensionless Reynolds number Re, which characterizes the laminar and turbulent flow regimes of a fluid, with Eq. 2.7 where  $\rho$  is the mass density,  $u_x$  is the flow density in x-axis direction and  $\mu$  is the viscosity [4].

$$\operatorname{Re} = \frac{\rho u_x}{\mu}$$
 2.7

Subsequently, the boundary layer thickness  $\Delta$  can be calculated with Eq. 2.8 where x is the distance from the inlet in flow direction.

$$\Delta = \sqrt{\frac{x}{\text{Re}}}$$

In order to proceed a coating process as efficient as possible it is necessary to know the deposition rate limiting mechanisms. The deposition rate can be calculated by the Arrhenius law and depends on temperature as can be seen in Eq. 2.9.

Deposition ~ rate = 
$$A * \exp\left(\frac{-E_a}{RT}\right)$$
 2.9

where A is a constant,  $E_a$  is the apparent activation energy, R is the gas constant and T is the deposition temperature. According to this, the Arrhenius plot in Fig. 2.3c shows different deposition rate limiting mechanisms which are represented by the different slopes, i.e. different activation energies. This plot shows principally that the deposition rate increases with increasing temperature. However, due to the

dependence of the surface processes from the deposition temperature at low temperatures, the surface chemical kinetics limits the deposition rate substituted by the slope in Fig. 2.3c region I. At higher temperature, the kinetic process goes on very fast so that the mass transport is the limited step characterized by Fig. 2.3c, region II [2].

The transition between the different limiting mechanisms also depends on the deposition pressure (Fig. 2.3). In case of low deposition pressure, the gas velocity increases as can be seen in Fig. 2.3a. Consequently, the boundary layer is very thin and the reactants can easily reach the surface which causes that the surface control mechanisms determine a wider temperature range. With increasing pressure the boundary layer thickness increases (Fig. 2.3b). Hence, mass transport, i.e. the diffusion rate through the boundary layer becomes dominating [4, 8, 9].



Fig. 2.3: Regions of mass transport and surface kinetics control at different pressures (P1<P2<P3) [4, 9].

#### 2.1.4 Evolution of film structure

Many important properties of polycrystalline thin films depend on their microstructure which can be influenced by the deposition parameters. The crucial steps during the deposition process are nucleation and growth of isolated crystals on a substrate surface, coalescence (forming a continuous thin film) and grain structure evolution during thickening as can be seen in Fig. 2.4 [10].



Fig. 2.4: Overview of grain structure evolution during deposition of polycrystalline thin films [10].

An important parameter during the nucleation step is the critical radius of the nuclei r<sup>\*</sup> which is given by Eq.2.10, where  $\gamma$  is the surface energy per unit area and  $\Delta G_v$  corresponds to the change in chemical free energy per unit volume. If the nucleus achieves the critical size, the further growth lowers the nuclei energy, i.e. the critical free energy barrier for nucleation has been overcome. The correlation between the critical radius r<sup>\*</sup> and the free energy barrier  $\Delta G^*$  of nuclei is displayed in Fig. 2.5 [7]. The critical free energy barrier can be calculated as demonstrated in Eq. 2.11.

$$r^* = \frac{-2\gamma}{\Delta G_{\rm v}}$$
 2.10



Fig. 2.5: Free energy change ( $\Delta G$ ) as a function of cluster (r\*>r) or stable nucleus (r>r\*) size [7].

A decreasing energy barrier leads to a higher nucleation rate which encourages the coalescence process. The nucleation rate N\* can be calculated using the Boltzmann factor k, the density of all possible nuclei sites  $n_s$ , the temperature T and the change of the free Gibbs energy. Eq.2.12 shows that the nucleation rate decreases with increasing temperature [7].

$$N^* = n_s * \exp\frac{-\Delta G^*}{kT}$$
 2.12

The nuclei grow until they contact and cover the surface completely. The growth mechanisms are responsible for the surface topography and occur either at discrete crystals dispersed on the substrate surface (Fig. 2.6a-b) or the growth is part of a polycrystalline structure (Fig. 2.6c-d) as documented by Barna et al. [11, 12]. Considering the first mechanism, the intersection between the substrate and the crystal side face is active (Fig. 2.6a) and the nucleation takes place at the top of the crystal while in Fig. 2.6b the intersection is passive and takes place on the crystal, side face. Consequently, the coalescence is controlled by the minimization of the substrate-interface energy.

The second mechanism shows the dependency of impurities such as doping elements on the monolayer growth of crystals. A rather pure grain boundary in Fig. 2.6c leads to hills along grain boundaries while in Fig. 2.6d contaminated grain boundaries are inactive and tend to form grooves, decorated by small particles [11-13].



Fig. 2.6: Types of crystal growth in polycrystalline thin films: (a) and (b) growth of dispersed individual crystals on the substrate surface, the intersection between the substrate and the side crystal faces are active (a) and passive (b) in the monolayer nucleation, (c) and (d) role of grain boundaries in the growth of crystals as parts of a polycrystalline matrix, pure grain boundary active in the monolayer nucleation (a), contaminated grain boundary passive in the monolayer nucleation (b) [11].

Considering two islands, coarsening via surface atom diffusion driven by the lowering of surface energy can be observed. Low surface diffusivities lead to smaller grains at coalescence. Due to differences in size, surface energy or interface energy, growing and shrinking of islands can be observed as schematically illustrated in Fig. 2.7 [10, 14].



Fig. 2.7: Coarsening resulting from the coalescence of two islands [10].

Depending on the affinity between coating and substrate atoms, the further grain growth may occur according to one of three modes (Fig. 2.8):

- Island growth (Volmer-Weber)
- Layer growth (Frank-van der Merwe)
- Mixed layer-island growth (Stranski-Krastanov)

The island growth (Volmer-Weber growth) occurs if the atom-atom bonding energy is higher than the atom-substrate energy. The smallest stable cluster nucleates on the substrate surface and grows in three dimensions to form islands. The layer growth mechanism (Frank-van der Merwe) is favored when the atoms are more strongly bonded to the substrate which leads to epitaxial growth and stacked monolayers. The Stranski-Krastanov growth mechanism is a combination of the two above mentioned growth modes. In this case, after the deposition of a few monolayers the layer growth becomes unfavorable and islands are formed [7, 15].



Fig. 2.8: Basic modes of thin film growth [7].

A basic model to achieve a desired structure depending on the deposition temperature was developed by Movchan and Demichshin and is called structure zone model (SZM). The model constructed by the compilation of numerous experiments was extended by Barna and Adamik [11]. This advanced SZM considers the contribution of impurities in conjunction with the homologous temperature  $T_s/T_m$ , where  $T_s$  is the substrate temperature and  $T_m$  is the melting point of the film material. Fig. 2.9 shows the dependency of the structure from the impurity content and the homologous temperature.

Zone I is characterized by a low substrate temperature whereby the nucleation density is very high. Due to the marginal grain boundary migration and negligible coalescence, the grains grow only in vertical directions. Consequently, a fibrous structure can be observed with high dislocation density and porous grain boundaries. Low amounts of impurities will lead to smaller columns, while medium and high amounts of impurities will limit the grain growth.

Zone T is determined by increasing grain boundary migration due to a higher substrate temperature. The competitive growth of the differently oriented neighboring

crystals develops V-shaped crystals which are typical for CVD. At higher temperatures, the grain boundary mobility increase and the grains grow along the substrate surface.

Zone II represents a high homologous temperature where grain boundary migration becomes decisive. The structure consists of columnar crystals with similar orientation. Large grains with a favorable orientation grow at the expense of smaller grains. Impurities inhibit the grain boundary migration which leads to a shift of zone II to higher temperatures. This temperature range is called zone III.

Zone III only exists at very high impurity concentration. Due to a periodical blocking of the grain boundary by impurities, Zone III is represented by equiaxed three dimensional (globular) grains. This structure is a consequence of the presence of inhibitors and can be formed at every substrate temperature [11, 13, 14, 16].



Fig. 2.9: Ideal (a) and real structure zone models for low (b), medium (c) and high (d) impurity concentrations [13].

# 2.2 Aluminum Oxide

### 2.2.1 Properties of Al<sub>2</sub>O<sub>3</sub>

 $AI_2O_3$  offers various advantageous properties, which makes it useful for cutting applications. Although  $AI_2O_3$  is not as hard as TiC coatings at room temperature, it becomes already harder than TiC above 800 °C as can be seen in Tab. 2.2.  $AI_2O_3$  is characterized by further advantageous properties such as good corrosion resistance, high dielectric strength, high resistance to impurity diffusion, low dissolution rate into iron based materials and low thermal conductivity which decreases with increasing temperature. Hence,  $AI_2O_3$  provides excellent protection against wear and raises essentially the life time of cemented carbide cutting tools in continuous cutting operation, i.e. turning [17, 18].

Constituent	HV (kg mm <sup>-2</sup> )		The condu (W m	rmal ictivity <sup>-1</sup> K <sup>-1</sup> )	Chemical o wear rates Ti	lissolution relative to C	Linear thermal expansion coefficient ( x 10 <sup>-6</sup> K <sup>-1</sup> )
T <sub>Room</sub>		1073 K	773 K	1273 K	773 K	1373 K	
TiC	3200	500 - 700	37	41	1	1	7.6
TiN	2000	700 - 800	23	26	1.8 x 10 <sup>-3</sup>	2.2 x 10 <sup>-3</sup>	9.4
$AI_2O_3$	2370	900 - 1200	13	6	8.9 x 10 <sup>-11</sup>	4.1 x 10⁻⁵	8.0

Tab. 2.2: Physical (bulk) properties of TiC, TiN and Al<sub>2</sub>O<sub>3</sub> [18].

### 2.2.2 Crystal structures and modifications of Al<sub>2</sub>O<sub>3</sub>

Various crystallographic modifications of  $AI_2O_3$  can be synthesized. Tab. 2.3 shows data of the  $\alpha$ ,  $\kappa$  and  $\gamma$  modification which can be deposited in a controlled way by CVD. Further modifications of  $AI_2O_3$  are  $\delta$ ,  $\theta$ ,  $\sigma$ ,  $\eta$  and  $\chi$  [1, 5, 18].

 $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the thermodynamically stable phase with a trigonal structure which has an ABAB stacking sequence of almost close packed oxygen ions along the c-axis. The microstructure consists of equiaxed grains which are randomly oriented. The grains include a large number of dislocations and pores whereas the latter were mainly located at grain boundaries. The density of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is 3.96 g/cm<sup>3</sup> [5, 18-20].

The orthorhombic  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> structure possesses an ABAC stacking of almost close packed oxygen ion planes. The  $\kappa$  phase has a smaller grain size compared to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Furthermore,  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is characterized by columnar twinned grains which are dislocation and pore free. The preferred growth direction is along the c-axis. The density of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is 3.67 g/cm<sup>3</sup> [5, 20].

A comparison of both phases shows that  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is tougher than  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> due to the smaller grain size and porosity of the  $\kappa$  phase [5]. Further differences are the number of atoms per primitive unit cell n of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (n = 10) and  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> (n = 40). The higher n, the lower porosity and the smaller density of point defects in the  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> phase lead to crystals with more complex structure and consequently to lower thermal conductivity which is reduced by a factor of ~3 compared to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as can be seen in Fig. 2.10 [21].

The metastable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase has a cubic structure and is based on a face centered cubic ABCABC stacking sequence of oxygen. It is defined as a defect cubic spinel structure with vacancies on a fraction of the cation positions. The aluminum ions fill out the octahedral and tetrahedral positions.

 $\eta$ -Al<sub>2</sub>O<sub>3</sub> is also based on a face centered cubic structure whereby it is very similar to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase [5].

Tab. 2.3: Properties of stable and metastable CVD Al<sub>2</sub>O<sub>3</sub> phases [1].

	α-Al <sub>2</sub> O <sub>3</sub>	к-Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Stability	Stable	Metastable	Metastable
Crystal system	Trigonal	Orthorhombic	Cubic
Space group	$D_3^6 d = R \bar{3}c$	Pna2 <sub>1</sub>	Fd3m
Lattice parameters (Å)	Hexagonal (h):	a = 4.8351	a = 7.92
	a = 4.7587, c = 12.9929, n = 6	b = 8.3109	
	Rhombohedral (R):	c = 8.9363	
	$A = 5.12, \alpha = 55.17^{\circ}, n = 2$		
Al atoms in unit cell	12(h)/4(R)	16	63/3
O atoms in unit cell	18(h)/6(R)	24	32

Data for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> cell is given in both hexagonal (h) and rhombohedral (R) systems.





Due to the strong temperature dependency of the metastable  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> phase, a phase transformation into the stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase will occur at relatively high temperature, for example during the cutting process (Fig. 2.11) [18]. This transformation results in a volume contraction in the range of 8% which possibly deteriorates the adhesion of the  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> [1, 18]. Hence, the production of high-quality  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is beneficial for the cutting industry as no transformation can influence the performance of the coating [1, 18].



Fig. 2.11: TTT diagram for  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> [18].

#### 2.2.3 Deposition of Al<sub>2</sub>O<sub>3</sub> films

The deposition of  $AI_2O_3$  is mainly influenced by the different gas compositions, temperatures and pressures. In this thesis two different types of carrier gas compositions were investigated, first a gas composition of  $H_2/Ar/CO_2/N_2$  and second a gas mixture of  $H_2/CO_2$ . These gas compositions have been suggested in different papers, e.g. in [22] the HCl/H<sub>2</sub>/Ar/CO<sub>2</sub> system is discussed while the HCl/H<sub>2</sub>/CO<sub>2</sub> system is reported in [19, 23-25].

The basic precursor material for producing high quality  $AI_2O_3$  coatings is AI granulate which are evaporated by HCI. The produced  $AICI_3$  reacts with  $CO_2$  and  $H_2$  in several steps to  $AI_2O_3$  (Eq. 2.12).

Surface reaction: 
$$2AlCl_3 + 3H_2O \leftrightarrow Al_2O_3 + 6HCl$$
 2.12

The reaction paths for producing an  $AI_2O_3$  coating from  $AICI_3/H_2/CO_2$  consists of the undesired homogeneous gas reactions which result in powder and the heterogeneous gas phase reactions which lead to the formation of solid species within the reactor, as can be seen in Fig. 2.12.



Fig. 2.12: Schematic illustration of the key steps in a CVD process [26].

The overall reaction for the deposition of  $Al_2O_3$  seems to proceed through a free radical chain mechanism [27]. The H<sub>2</sub>O, essential for decomposition of AlCl<sub>3</sub>, can be generated by several ways. Eq. 2.13 shows the formation of H<sub>2</sub>O by the water gas shift reaction. Important reactions for producing H<sub>2</sub>O are also given in Eq. 2.14 - Eq. 2.16 [17]. A detailed overview about the overall reaction divided in different reactions occurring during the deposition process is visualized in Fig. 2.13 [28].

Gas reaction: 
$$H_2(g) + CO_2(g) \leftrightarrow H_2O(g) + CO(g)$$
 2.13

$$H_2 + OH \leftrightarrow H_2O + H$$
 2.14

$$HCl + OH \leftrightarrow H_2O + Cl$$
 2.15

$$AlO + H_2 \leftrightarrow Al + H_2O$$
 2.16



Fig. 2.13: Deposition of Al<sub>2</sub>O<sub>3</sub> on the substrate surface out of gaseous and adsorbed species [28].

The decomposition rate of  $AICI_3$  into  $AICI_2$  and AICI is influenced by many factors, e.g. the decomposition rate rises with increasing H<sub>2</sub> amount (Fig. 2.14) and decreases if a significant amount of HCI (Fig. 2.15) is in the gas mixture. Furthermore, an increasing amount of H<sub>2</sub> causes a faster desorption of the reaction products and leads to higher reactivity [29]. The influence of CO<sub>2</sub> on the decomposition rate depends on different parameters like temperature and flow rate. Further investigations according influences of  $AI_2O_3$ , H<sub>2</sub>, partial pressure and temperature on deposition rate are illustrated by Kim et al. [30].



Fig. 2.14: Calculated AlCl<sub>3</sub> decomposition at 100 mbar and 1323 K for a mixture of 2 mol% AlCl<sub>3</sub> + 2 mol%  $CO_2$  in Ar (full line) and for a mixture of 2 mol% AlCl<sub>3</sub> + 2 mol%  $CO_2$  in H<sub>2</sub> (dashed line). The ratio of time dependent concentration [AlCl<sub>3</sub>] and initial concentration [AlCl<sub>3</sub>]<sub>0</sub> describes the decomposition [31].



Fig. 2.15: AICl<sub>3</sub> profiles, feed gas (mol%): 4 CO<sub>2</sub>, 60 H<sub>2</sub>, variable HCl, flow rate 20 slh. The decreasing mole fraction of AICl<sub>3</sub> shows its decomposition [27].

# 2.3 Doping of Aluminum Oxide

As mentioned in chapter 2.1.3, already low amounts of an additional coating constituent may lead to a change in microstructure. Consequently, a lot of properties of  $AI_2O_3$  such as hardness, strength, optical properties, electrical and thermal conductivity can be influenced by doping elements [4].

Yoshida et al. [32] investigated the influence of cation doping with different doping elements and increasing temperature on the grain boundary diffusivity in  $Al_2O_3$  coatings (Fig. 2.16). It should be pointed out that even a small amount of doping elements changes the boundary diffusion coefficient and consequently the high temperature creep of  $Al_2O_3$ .



Fig. 2.16: An Arrhenius plot of the grain boundary diffusivity against inverse temperature in undoped  $AI_2O_3$  and 0.1 mol % cation doped  $AI_2O_3$  [32].

#### 2.3.1 Selected Dopants

The choice of the precursor elements was supported by the previous diploma thesis of Czettl [28] and by the Ph. D. thesis of Kathrein [28, 33]. Based on these studies, the investigated doping elements were selected and further dopants with similar properties were added. Tab. 2.4 gives an overview about the oxides of the used elements and their applications.

Oxide		T <sub>m</sub> [34]	Applications	
	Aluminum oxide	2054	Coating for carbide tools Semiconductor industry	[4]
	Strontium oxide	2530	Thermoluminescence Photoluminescence	[35]
	Yttrium oxide	2690	Photovoltaic devices, Lasers Magnetic recording devices High temperature applications	[36]
_	Manganese oxide	1650	Optical effects in ceramic industry through pink pigments	[37]
_	Niobium oxide 1937 Optical layers Sensors		Optical layers Sensors	[4]
	Tantalum oxide	1880	High dielectric - constant capacitors Gate insulators in MOS devices Optical coatings, Anti-reflection coatings	[4]
	Silicon oxide	1713	Oxidation protection of stainless steel in nuclear reactors Etch barriers, Intermetallic dielectrics Passivation layers and doping barriers in semiconductor devices	[4]

Tab. 2.4: Overview about applications of oxides.

Decisive precursor properties are melting temperature  $T_m$  and boiling temperature  $T_b$  of the chloride as they give a first hint whether an experimental approach could succeed or not. Fig. 2.17 shows chloride precursors with the respective melting and boiling temperature which can be classified into high-melting chlorides (MnCl<sub>2</sub>, YCl<sub>3</sub>, SrCl<sub>2</sub>), low-melting chlorides (TaCl<sub>5</sub>, NbCl<sub>5</sub>) and liquid chlorides (SiCl<sub>4</sub>) compared to metallic Al which will be chlorinated with HCl at 300 – 650 °C.



Fig. 2.17: Boiling and melting temperature of the different chlorides and aluminum.

A further guideline for the correct deposition temperature was given by vapor pressure curves of the chlorides which were calculated with the HSC-chemistry software [38]. Fig. 2.18 shows the different chlorides and the respective vapor pressures depending on increasing temperature. SrCl<sub>2</sub>, YCl<sub>3</sub> and MnCl<sub>2</sub> exhibit low vapor pressure values at temperatures up to 1300°C. The chlorides of Ta and Nb show an increasing vapor pressure at their melting points (cf. Fig. 2.17). SiCl<sub>4</sub> exhibits the highest vapor pressure at low temperatures, because it is already liquid at room temperature. The fact that deposition experiments could only be performed under atmospheric pressure limits the possibilities for volatilization in the reactor. Further experiments using a production plant with low pressure should allow increased volatilization, lower temperatures and easier precursor transportation.



Fig. 2.18: Vapor pressure of the different chlorides, calculated using HSC-chemistry.

#### 2.3.2 Strontium Oxide

The binary phase diagram of SrO and Al<sub>2</sub>O<sub>3</sub> in Fig. 2.19 shows the stable oxides 3SrO.Al<sub>2</sub>O<sub>3</sub>, SrO.Al<sub>2</sub>O<sub>3</sub>, SrO.2Al<sub>2</sub>O<sub>3</sub> and SrO.6Al<sub>2</sub>O<sub>3</sub> which is similar to the well known CaO-Al<sub>2</sub>O<sub>3</sub> system [35]. The mentioned mixtures can be obtained by controlled cooling from the melt, slow heating the precursor powders or already after grinding the amorphous powders. A further stoichiometric compound of SrO and Al<sub>2</sub>O<sub>3</sub> investigated by Massazza et al. [39] is 4SrO.Al<sub>2</sub>O<sub>3</sub> which forms an  $\alpha$  modification between 1320 °C and 1690 °C and a  $\beta$  modification between 1125 °C and 1320 °C. In spite of its high ionic radius, strontium stabilizes the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure. The monoclinic SrO.Al<sub>2</sub>O<sub>3</sub> crystallizes out of the amorphous phase at 917°C. At 650 °C the monoclinic structure transform s into a hexagonal polymorph structure which is stabilized at room temperature by cations like calcium, silicon or excess aluminum [35].



Fig. 2.19: SrO-Al<sub>2</sub>O<sub>3</sub> diagram, after Masazza [39].

Strontium lowers the grain boundary diffusivity in dependence of the temperature as can be seen in Fig. 2.16. This could lead to smaller grain size during coalescence as explained in chapter 2.1.4 and illustrated by Yoshida et al. [32].

#### 2.3.3 Yttrium Oxide

The binary phase diagram of  $AI_2O_3$  and  $Y_2O_3$  was investigated by many experiments. Mao et al. [40] compared calculated and experimental data which is displayed in Fig. 2.20. The system exhibits three intermediate phases. The first phase, yttrium aluminum garnet (YAG,  $Y_3AI_5O_{12}$ ), is stable in the range of low  $Y_2O_3$  content and occurs during grain growth. Due to a substitution process of the larger Y atoms by Al atoms in the  $AI_2O_3$  matrix, a phase transformation to the Y aluminum perovskite phase (YAP, YAIO<sub>3</sub>) can be observed at  $Y_2O_3$  mole fraction around 0.5. The formation of YAP takes place at 1350 K just like the third phase (YAM,  $Y_4Al_2O_9$ ) which consists of a monoclinic structure [36, 40-46]. However, this temperature region is not represented in the phase diagram.



Fig. 2.20: Phase diagram of the  $Y_2O_3$ -Al<sub>2</sub>O<sub>3</sub> system [40].

Stoichiometric  $Y_2O_3$  is characterized by a white color, higher toughness and fracture energy compared to the non-stoichiometric  $Y_2O_3$  which is black if it is exposed to high temperatures and reducing atmosphere. Furthermore, Y-doping causes an increasing corrosion resistance, but also an increased porosity and creep rate in the  $Al_2O_3$  [41, 42].

#### 2.3.4 Manganese Oxide

The binary phase diagram of MnO and  $Al_2O_3$  published by Eriksson et al. [47] is shown in Fig. 2.21. It exhibits the MnO- $Al_2O_3$  phase which is stable in the range of  $67 - 72 \mod 8 Al_2O_3$  up to 1835 °C. An eutectic point exists at 59 mol% MnO and 1530 °C. Manganese cations which are dissolved in the corundum lattice can cause a pink color in the  $Al_2O_3$  coating. Especially a higher amount of Mn(III) increases the intensity of the color [37]. Sathiyakumar et al. [48] have shown that the hardness and the flexural strength increases for a Mn-content above 0.5 wt.% [47, 48].



#### 2.3.5 Niobium Oxide

According to the binary phase diagram shown in Fig. 2.22, three intermediate phases occur. The most stable phase in this system is NbO which exists up to 1945 °C. The  $Al_2O_3-Nb_2O_5$  system in Fig. 2.23 exhibits two phases. The  $AINbO_4$  shows good bonding properties between TiC and  $Al_2O_3$  and forms together with  $Al_2O_3$  a two phase field at low Nb content [49].



Fig. 2.22: Niobium oxygen system [50].



Fig. 2.23: Binary phase diagram  $AI_2O_3$ - $Nb_2O_5$  [49].

#### 2.3.6 Tantalum Oxide

Tantalum oxide coatings (Ta<sub>2</sub>O<sub>5</sub>) are transparent and possess a relatively high melting point of 1852 °C. The binary phase diagram  $AI_2O_3$ -Ta<sub>2</sub>O<sub>5</sub> documented in Fig. 2.24 shows a wide range of intermediate phases. Due to its good bonding properties at an  $AI_2O_3$ /TiC-interface due to similar lattice parameters as like Nb,  $AITaO_4$  offers a high thermal stability over a wide range of temperatures.



Fig. 2.24 Binary phase diagram Al<sub>2</sub>O<sub>3</sub>-Ta<sub>2</sub>O<sub>3</sub> [49].

#### 2.3.7 Silicon Oxide

Due to the high thermal and chemical stability of  $SiO_2$ , its deposition is very important for the production of protective coatings in electronics. Especially mullite with a chemical composition ranging from  $3Al_2O_3.2SiO_2$  to  $2Al_2O_3.SiO_2$  exhibits very attractive properties, e.g. high bending strength and good hot corrosion resistance. Furthermore, mullite possesses a thermal expansion coefficient of  $5.5 \times 10^{-6}$  K<sup>-1</sup> [34, 51] which is similar to Mo, ranging from  $5 \times 10^{-6}$  K<sup>-1</sup> to  $7 \times 10^{-6}$  K<sup>-1</sup> at 100 °C – 1000 °C [34, 51, 52]. Fig. 2.25 shows a SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system containing the mullite phase which is the only stable compound in this system. The high thermal resistance can be explained by the relatively high melting point of 2123 °C. Mullite crystallizes in an orthorhombic structure for a fraction of ~60% Al<sub>2</sub>O<sub>3</sub>. At lower Al<sub>2</sub>O<sub>3</sub> contents, a cristobalit modification of SiO<sub>2</sub> can be observed which has one of the lowest oxygen diffusion coefficients among the group of oxides [53].



Sotirchos et al. [17] reported that the amount of  $AI_2O_3$  within the  $AI_2O_3$ -SiO<sub>2</sub> coating system increases for increasing deposition temperature. Fig. 2.26 shows this dependency which allows to adjust the necessary temperature for a desired composition.





# 3 Experimental

The different melting temperatures and boiling temperatures of the chlorides make different experimental setups necessary, i.e. different precursor handling, precursor transport and volatilization reactors. The following experimental setup bases upon the previous diploma thesis by Czettl [28] where the furnace tube was horizontal compared to the vertical alignment within this work. The used reference gas mixture for the experiments was a downscaling of a gas composition used in a production plant [55].

# 3.1 CVD equipment

The experiments were performed in a vertical hot wall reactor manufactured by Reetz which measured 1200 mm in length and 51 mm in inner diameter of the working tube. The heating system consists of three separate controllable molybdenum heating coils which were flushed with argon in order to avoid oxidation. Following, this plant is shortly named as "Reetz furnace" within this work.

### 3.1.1 Experimental Configuration

A graphite tube with 553 mm in length and 50 mm in diameter was used as specimen carrier and placed in the bottom of the reaction chamber. The substrates were positioned on four disks whereas the bottom disk was loaded with four samples and the other three disks carried only one sample. The distance between the disks was 27 mm (Fig. 3.1).

A Mo-reactor consisting of a reaction chamber and three tubes was placed in the first, topmost heating zone of the Reetz furnace. Through pipe #1 the hydrochloride vapor is transported via Ar gas and hydrogen into the reactor chamber where aluminum granulate or other precursor materials are chlorinated, vaporized and transported to the substrate. Nitrogen and carbon dioxide flow through pipe #2 which was arranged in the center of the reactor. Pipe #3, which ended behind the reactor, provided an Ar gas flow in order to prevent a backflow of gases. A thermocouple reached into the reactor and controlled the temperature within the reaction chamber (see orange tube, Fig. 3.1b).

Strontium chloride (SrCl<sub>2</sub>), yttrium chloride (YCl<sub>3</sub>) and manganese chloride (MnCl<sub>2</sub>) were placed in a molybdenum crucible close to the gas outlet of the reactor as seen in Fig. 3.2.

For one experiment, manganese chloride ( $MnCl_2$ ) was also placed on the top of the graphite tube (L5, Fig. 3.3) which allows higher volatilization temperature and minimizes the distance between sample and precursor.



Fig. 3.1: Reetz furnace – Single reactor assembling (a...Reetz furnace, b...Mo-reactor, c...sample alignment, L...level)



Fig. 3.2: Precursor emplacement in the reactor.



Fig. 3.3: Precursor emplacement on the graphite tube close to the substrates.

#### Temperature gradient

The temperature gradient was measured via thermocouples and process temperature control rings (PTCR), first in standard and second in hydrogen gas atmosphere. Fig. 3.4 shows the temperature for each specimen position inside the Reetz furnace, where the temperature decreases from level L4 to level L1. The position of the PTCR was related to the bottom flange of the furnace.



Fig. 3.4: Temperature profile in the Reetz furnace at the respective specimen positions.

#### 3.1.2 Additional reactor

#### 3.1.2.1 Solid chloride reactor

A second reactor was necessary to enable the experiments using precursors with lower vaporization temperatures than the Al-chlorination temperature (Fig. 3.5). It was very important to position the second reactor, which was controlled by a thermocouple, as near as possible to the Reetz furnace to keep the connecting feed line as short and as hot as possible. The feed line was heated to 210  $^{\circ}$ C by an electric belt in order to avoid coating deposition and clogging in the feed line. In the middle of the second reactor a molybdenum crucible ring was positioned and filled with NbCl<sub>5</sub> or TaCl<sub>5</sub>. A hydrogen carrier gas flew through a central tube, which ends close to the crucible ring within the reactor and transported the precursor into the Reetz furnace.



Fig. 3.5: Double reactor configuration - solid chloride.

#### 3.1.2.2 Glass – bubbler

For the liquid SiCl<sub>4</sub> and once for the solid NbCl<sub>5</sub> precursor, a glass bubbler was positioned as near as possible to the Reetz furnace for the same reasons which were described in section 3.1.2.1 (Fig. 3.6). H<sub>2</sub> was piped into a glass vessel which was filled with the liquid precursor. The liquid was evaporated by heating a water quench with a heater. Evaporation could be observed in-situ, because the whole bubbler was transparent.



Fig. 3.6: Double reactor configuration – liquid chlorides.

# 3.2 Substrates and precursors

#### 3.2.1 Precursor materials and gases

Tab. 3.1 shows the used materials as well as the carrier gases with the corresponding purity.

Tab. 3.1:	Condition	of the	precursor	materials.
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Element	Purity	state of matter	shape
Aluminium	AI (>99.9%)	solid	granules
Strontium	SrCl <sub>2</sub> (>99.9%)	solid	salt
Yttrium	YCl <sub>3</sub> (>99.9%)	solid	salt
Manganese	MnCl <sub>2</sub> (>96%)	solid	salt
Niobium	NbCl <sub>5</sub> (>99%)	solid	salt
Tantalum	TaCl <sub>5</sub> (>99%)	solid	salt
Silicon	SiCl <sub>4</sub> (>99%)	liquid	salt
Methane	CH <sub>4</sub> (>99.5%)	gaseous	-
Ammoniac	NH <sub>3</sub> (>99.99%)	gaseous	-
Nitrogen	N <sub>2</sub> (>99.99%)	gaseous	-
Hydrogen	H <sub>2</sub> (>99.99%)	gaseous	-
Carbon monoxide	CO (>99.99%)	gaseous	-
Carbon dioxide	CO <sub>2</sub> (>99.99%)	gaseous	-
Argon	Ar <sub>2</sub> (>99.98%)	gaseous	
Hydrogen chloride	HCI (>99.99%)	gaseous	-

#### 3.2.2 Substrate material

Mo and cemented carbide substrates with three kinds of precoatings were used within this work:

Cemented carbide cutting inserts of Ceratizit grade S40T with a SNUN 120412 geometry, according to ISO 1832, precoated at two different deposition temperatures in a production plant and molybdenum discs without precoating, which measured 16 mm in diameter and 4 mm in thickness. The composition of the different substrates and their abbreviation which identifies them within this work is given in Tab. 3.2.
Identification	Substrate	Precoating	Particularities
A	cemented carbide:	TiCN/TiN	-
В	77 wt.% WC; 11 wt.% Co;		$T_{deposition}C < T_{deposition}B$
С	8 wt.% (Ta,Nb)C; 4 wt.%TiC		refined structure
Мо	Molybdenum	-	-

Tab. 3.2: Composition of the substrate material.

## 3.2.3 Sample preparation and deposition procedure

First of all, the substrates were grinded and polished. Previous to the batching of the samples into the furnace, the substrate material was weighted. For each deposition run, four substrates (A, B, C, Mo) were placed on level one and one A-sample was placed on the levels two to four. After connecting the gas supply, the working tube was evacuated with a vacuum pump, filled with Ar and heated up to the desired deposition temperature (Ar and H<sub>2</sub> flushing). Subsequently, the coating process started with the chlorination of AI, which was started with the transport of HCI and carrier gas through the Mo-reactor. After five minutes of chlorination,  $CO_2$  was introduced into the furnace. In general, the doping of  $AI_2O_3$  was delayed depending on the precursor element for 10 - 30 minutes.

The deposition runs were identified by the abbreviation RD and the corresponding deposition run number, e.g. RD43, which was the first run of this thesis as previous works are also included in the serial number.

The deposition time was kept constant at three hours except RD51, RD62 and RD78. Detailed coating recipes of the deposition runs are given in appendix. Finally, the coated samples were dissembled, weighted and the mass gain was calculated.

## 3.3 Coating characterization

## 3.3.1 Gravimetric analysis

The gravimetric analysis of the uncoated and coated samples and the precursor consumption were performed using a Mettler AT Delta Range 261 precision balance with an accuracy of  $\pm 0.1$  mg.

## 3.3.2 Light optical microscopy

The coated specimens were grinded and the resulting cross-section was polished in order to measure the coating thickness. A light optical microscope (Nikon Epiphot 300) with an additional LEICA DFC 420 camera was used in combination with the software "image access" [56].

## 3.3.3 Scanning electron microscopy

A FEI Quanta 200 scanning electron microscope (SEM) was used to image the surface of the deposited layers and the fracture cross-sections. The acceleration voltages were set between 20 and 30 kV and the working distance was approximately 10 mm. The micrographs were gained with a secondary electron detector (SE), back scattered electron detector (BSE) and with a combination of both detectors (mixed mode, MX).

The chemical analysis was conducted with energy dispersive X-ray spectroscopy (EDX, Oxford Instruments INCA) during the SEM investigation. For EDX measurements, the working distance was also set to ~10 mm and an acceleration voltage of 30 kV was used. It has to be mentioned that the samples were contacted with a copper adhesive strip in order to minimize charging of the coating.

## 3.3.4 Glow discharge optical emission spectroscopy

The concentration depth profiles of the elements were characterized by glow discharge optical emission spectroscopy (GDOES) with a Jobin-Yvon Horiba JY10000RF facility. GDOES possesses significantly lower detection limits, compared to EDX and allows analyzing the sample underneath the surface (concentration depth profiles up to several 10  $\mu$ m depth) [57]. Only qualitatively measurements were performed, in order to clarify the incorporation of dopants.

## 3.3.5 X-ray diffraction analysis

Glancing angle X-ray diffraction analysis (GAXRD) was used to determine the phases and crystal structures of the films. The XRD studies were performed on a Panalytical X'Pert Pro diffractometer using copper  $K_{\alpha}$ -radiation and a flat graphite monochromator. The texture coefficients (TC) for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coatings were calculated according to Eq.3.1 where I(hkl) the measured intensity of the respective (hkl) reflection, n is the number of considered reflections and I<sub>0</sub>(hkl) is the respective peak intensity according to the JCPDS file # 00-010-0173 [1].

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \left\{ \frac{1}{n} \sum \frac{I(hkl)}{I_0(hkl)} \right\}^{-1}$$
3.1

## 3.3.6 Nanoindentation

Hardness measurements were carried out on a UMIS nanoindenter with an additional DME Dualscope® DS45-40 AFM objective. The load frame compliance of this instrument is 0.2 nm/mN. A Berkovich indenter tip was utilized which is a frequently

used indenter shape in nanoindentation. The indentation load ranged from 10 mN to 30 mN and the corresponding indentation depth, as well as hardness and elastic modulus were analyzed with the IBIS software [58]. A schematic indenter assembling is shown in Fig. 3.7 and a typical load displacement curve can be seen in Fig. 3.8. The operation includes the following steps:

- The leaf spring system and the expansion of a Plumbum Zirconate Titanate (PZT) load actuator transmit the force to the indenter shaft.
- The leaf springs deflect if the indenter contacts the surface of the sample. This deflection is measured using the force linear variable differential transformer (LVDT).
- The separate displacement of the shaft relative to the stage is measured by the depth LVDT [59].



Fig. 3.7: Principle of an UMIS nanoindenter [59].



Fig. 3.8: Schematic of indentation load-displacement curve measured with a Berkovich indenter [60].

#### 3.3.7 Oxidation test

In order to check the oxidation properties of the  $Al_2O_3$  coatings on Mo-samples in air at different temperatures, the samples were placed in a high temperature Heraeus M110 muffle furnace. A literature survey helps for the choice of the suggestive temperature range [61]. The oxidation test was realized for 12 hours at 550 °C, 24 hours at 650 °C and 24 hours at 750 °C with an i ntermediate weighting which enables calculation of the oxidation rate.

## 4 Results and Discussion

The results of the experiments conducted within this thesis are first shown for undoped Al<sub>2</sub>O<sub>3</sub> coatings and then continued with doped aluminum. The investigations covered different carrier gas mixtures, doping elements (Nb, Y, Sr, Ta. Si, Mn) and additional gases (CH<sub>4</sub>, NH<sub>3</sub>). The table in the appendix offers a brief overview, containing all deposition temperatures, gas flow rates, evaporation rates, mass gain coating thickness as well as hardness and elastic modulus for selected samples. Furthermore, the configuration of the experimental setup is mentioned. Due to the extensive analysis caused by the investigations were limited to substrate and precoating type (see table Tab. 3.2), the investigations were limited to substrate C and Mo for all experiments performed after the deposition run RD60. Except mass gain and coating thickness measurements, which were performed for the levels L1 to L4, coating characterization was focused on level L1. For a better understanding of the following diagrams it should be keep in mind that the temperature increases from level L4 to L1 (cf. Fig. 3.4).

## 4.1 Aluminum oxide

## 4.1.1 Gas composition

For the coating experiments with different carrier gas mixtures,  $H_2$ , Ar, and  $N_2$  were varied as can be seen in the ternary diagram in Fig. 4.1. A standard gas composition was defined (RD48) and used as reference. The highest hardness value was measured for the deposition run RD47 with only  $H_2$  as carrier gas. Also the coatings deposited without Ar (RD46) or without  $N_2$  (RD63) showed a slightly increased hardness, compared to the reference coating (RD48). Within this variation, only one coating (RD45) showed a lower hardness value than the reference. Most experiments with doping elements were realized in a standard gas atmosphere, comparable to run RD48 and with  $H_2$  carrier gas comparable to RD47. Furthermore, the influence of additional CH<sub>4</sub> and NH<sub>3</sub> was examined.



Fig. 4.1: Ternary gas system with variation of  $H_2/Ar/N_2$  and the corresponding hardness value.

#### 4.1.2 Coating growth rate

For the different carrier gas mixtures (RD45-RD48, RD63), the growth rates at all levels are displayed in Fig. 4.2. The atmosphere which mainly consists of H<sub>2</sub> (RD47) shows the highest growth rates on all levels and the smallest variations. This increasing growth rate might be explained by a faster desorption of the by-products away from the substrate surface. Additionally, the higher H<sub>2</sub> amount could enhance the free radical chain mechanism which plays an important role for the formation of H<sub>2</sub>O and consequently for  $AI_2O_3$ , as explained in chapter 2.2.3. The obvious trend that the growth rate of a thermally activated reaction increases with increasing temperature is also clearly visible.



Fig. 4.2: Coating growth rates of undoped  $AI_2O_3$  with variation of  $H_2/Ar/N_2$ . Gas flow direction from right to left.

As mentioned in chapter 2.1.3, the Arrhenius plot is used to determine the rate limiting mechanism. In Fig. 4.3, the logarithm of the growth rates ln(R) is plotted against the inverse temperature. The activation energy (E<sub>a</sub>) has been calculated by Eq.4.1, where R is the gas constant and k the slope of the linear fit.



Fig. 4.3: Arrhenius plot for the Al<sub>2</sub>O<sub>3</sub> deposition with standard gas composition (RD48).

$$E_a = R * k = -63.19 kJ / mol$$
 4.1

where  $R = 8.314 \frac{J}{molK}$ 

Ruppi et al. [62] summarized a lot of activation energies of  $Al_2O_3$  coatings as can be seen in Tab. 4.1. The aberration from the comparable activation energies results

from the different influences like temperatures, pressures and gas compositions. The calculated activation energy (-63.19 kJ/mol) is in good agreement with literature, e.g. with the red framed deposition run which proceeds at similar parameters.

Reaction	Activation energy (kJ/mol)	Temp (K)	Pressure (mbar)	Doping	Reference	
Al <sub>2</sub> O <sub>3</sub> deposition	-82	1073-1273	50	Yes $(H_2 S = 1\%)$	This work	
Al <sub>2</sub> O <sub>3</sub> deposition	- 175	1073-1273	50	No	This work	
Al <sub>2</sub> O <sub>3</sub> deposition	-111	1073-1273	300	No	This work	
Al <sub>2</sub> O <sub>3</sub> deposition	-81	1073-1273	300	Yes $(H_2 S = 0.2\%)$	This work	
Al <sub>2</sub> O <sub>3</sub> deposition	-95.5	1003-1188	1013	No	29	
Al <sub>2</sub> O <sub>3</sub> deposition	-64.9	1173-1473	810	No	25	
Al <sub>2</sub> O <sub>3</sub> deposition	-131.0	1173-1473	61	No	25	
Al <sub>2</sub> O <sub>3</sub> deposition	-237.4	673-1273	1013	No	36	
Al <sub>2</sub> O <sub>3</sub> deposition	-150.7	1273-1423	67	No	30	
Al <sub>2</sub> O <sub>3</sub> deposition	-146.5	1273-1423	133	No	30	
Al <sub>2</sub> O <sub>3</sub> deposition	-100.5	1273-1423	533	No	30	
Water gas reaction	-326.6	1173-1323	1013	No	37	
Water gas reaction	-238.6	1148-1323	1013	No	38	

Tab. 4.1: Activation energies of different Al<sub>2</sub>O<sub>3</sub> deposition parameters [62].

## 4.1.3 Crystal structure

For alumina coatings deposited with varied carrier gas composition,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was the dominating alumina modification on all substrates. If only traces of an Al<sub>2</sub>O<sub>3</sub> polymorph were found, this is worked by parentheses.  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> was the main crystal phase only for N<sub>2</sub> -rich carrier gas composition (RD46) on Mo substrate. Frequently, small amounts of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> were detected on all substrate types while  $\eta$  were found only on A-substrates and  $\theta$  only occurs on Mo-substrates.

Tab. 4.2:  $Al_2O_3$  modifications formed on different precoatings and substrates with variation of  $H_2/Ar/N_2$ . Low phase contents are marked by parenthesis.

	Comment	А	В	С	Мо
RD45	standard + more $H_2$	α	α	α+(κ)	$\kappa + (\alpha + \theta)$
RD46	mainly N <sub>2</sub>	α+(κ)	α	α	$\alpha$ +( $\kappa$ + $\theta$ )
RD47	H <sub>2</sub>	α+(κ)	$\alpha + (\kappa)$	α+(κ)	α+(κ)
RD48	standard	$\alpha + \kappa + (\eta)$	$\alpha + (\kappa)$	α+(κ)	α+(κ)
RD63	mainly Ar	-	-	α	-

## 4.1.4 Coating morphology

Higher amounts of  $H_2$  (RD45),  $N_2$  (RD46) or Ar (RD63) (Fig. 4.4c-e) within the carrier gas mixture do not change the coating morphology significantly, when compared to the standard composition (RD48, Fig. 4.4a, b).



Fig. 4.4: SEM surface structure of undoped  $AI_2O_3$  with variation of  $H_2/Ar/N_2$ . The coating thickness is given in parenthesis.

The coating deposited with  $H_2$  carrier gas (RD47) shows a slightly coarser grain structure (Fig. 4.5a-c) compared to RD48. In general, the coating morphology is coarser on B-substrates compared to C-substrates, which is shown in Fig. 4.5a-b. This can be related to a finer structure of precoating C compared to B as mentioned in chapter 3.2.2. Also on Mo substrates, a slightly coarser grain structure can be observed (Fig. 4.5c) which is most pronounced for  $H_2$  atmosphere (RD47).



Fig. 4.5: SEM surface structure of undoped  $AI_2O_3$  on different precoatings and substrates with  $H_2$  gas only.

The fracture pattern of the  $H_2$  run (Fig. 4.6) reflects the V-shaped grain growth, mechanism which is already explained in chapter 2.1.4, and an oxide layer thickness which is similar to the precoated TiCN/TiCNO layer.



Fig. 4.6: SEM fracture cross-section of an undoped  $Al_2O_3$  coating on a TiCN precoating (substrate C) with  $H_2$  gas only.

## 4.2 Additional ammonia gas

The experiments with the additional NH<sub>3</sub> were carried out at different deposition temperatures. The NH<sub>3</sub> gas line was opened 30 minutes after deposition start. Consequently, a standard Al<sub>2</sub>O<sub>3</sub> layer (similar to RD48) with a thickness of ~ 0.5  $\mu$ m was deposited first.

#### 4.2.1 Coating growth rate

The addition of NH<sub>3</sub> causes the highest growth rates obtained within this work (Fig. 4.7). This can be explained by the higher reactivity of the nitrogen and hydrogen generated by the NH<sub>3</sub> decomposition. The influence of NH<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> deposition was investigated with thermodynamic calculations (HSC chemistry), where the Gibbs free energy is plotted versus temperature (Fig. 4.8). Compared to H<sub>2</sub> carrier gas (Fig. 4.8, red line), the increasing slope visible after NH<sub>3</sub> addition (Fig. 4.8, green line) indicates a tendency of increased Al<sub>2</sub>O<sub>3</sub> formation above 250 °C. The amount of NH<sub>3</sub> addition is comparable to deposition (Fig. 4.8, blue line). Additionally, the possibility of aluminum nitride formation or an Al-O-N-phase must be considered, which would also contribute to the increased growth rates. Similar thermodynamical calculations performed for nitride formation [26, 63], where the influence of highly reactive nitrogen which is also reported in literature [29] is shown.

According to the temperature gradient within the furnace (Fig. 3.4), a generally increasing deposition rate from L4 to L1 is visible. Already directly after deposition, some coatings show partial chipping (e.g. RD49) which might be caused by the high residual stress originating from the high coating thickness.



Fig. 4.7: Coating growth rates of undoped  $AI_2O_3$  coatings deposited with additional  $NH_3$  for different deposition temperature compared to the standard reference (RD48) ( $T_{RD80} < T_{RD60} < T_{RD60} < T_{RD49}$ ). Gas flow direction from right to left.



Fig. 4.8: Influence of temperature Gibbs free energy of reaction for the formation of  $AI_2O_3$  using  $H_2$  only (red solid line), NH<sub>3</sub> only (blue dashed line) and  $H_2$  +NH<sub>3</sub> (green dotted line).

## 4.2.2 Chemical composition

The deposition runs with additional  $NH_3$  (e.g. RD60) show an increased nitrogen amount within the outermost layer, compared to an undoped  $Al_2O_3$  coating, for example deposited with mainly Ar gas (RD63), see Fig. 4.9.



Fig. 4.9: GDOES plot of  $Al_2O_3$  coatings deposited with (a) additional  $NH_3$  gas (RD60) and (b) mainly Ar gas (RD63) on C substrates

## 4.2.3 Crystal structure

The additional NH<sub>3</sub> gas causes the formation of an amorphous phase (identified by XRD measurements); only RD49 which represents the highest coating temperature produces  $\eta$ -Al<sub>2</sub>O<sub>3</sub> phase on B and C and a mixed  $\gamma$ - and  $\kappa$ -phase on Mo (see Tab. 4.3). It is assumed that the amorphous phase partly results from the high growth rate and consequently insufficient time for nucleation and crystal growth.

Tab. 4.3: Al <sub>2</sub> O <sub>3</sub> modifications	formed on different precoatings and substrates with additional $NH_3$ gas
(T <sub>RD48</sub> <t<sub>RD60<t<sub>RD80<t<sub>RD50<t<sub>RI</t<sub></t<sub></t<sub></t<sub>	<sub>049</sub> ).

	Comment	А	В	С	Мо
RD49	standard + NH₃ T <sub>dep</sub> = 1050 ℃	_	η	η	γ+κ
RD50	standard + NH <sub>3</sub> T <sub>dep</sub> = 850 $^{\circ}$ C	amorphous	amorphous	amorphous	amorphous
RD60	standard + NH <sub>3</sub> T <sub>dep</sub> = 700 ℃	_	_	amorphous	amorphous
RD80	standard + NH <sub>3</sub> T <sub>dep</sub> = 600 $^{\circ}$ C	_	_	amorphous	_

## 4.2.4 Coating morphology

The SEM micrographs for the ammonia experiments are blurred because of the high coating thickness and a consequently high electrical charging. However, dome shaped features comprising of smaller spheres seem to be visible for all "ammonia" coatings (see Fig. 4.10).



Fig. 4.10: SEM surface structure of undoped  $AI_2O_3$  coatings on C substrates with additional  $NH_3$  gas  $(T_{RD49} < T_{RD49})$ .

## 4.3 Additional methane gas

## 4.3.1 Coating growth rate

Five experiments were performed with  $H_2$  carrier gas and additional methane gas flow rates in the range of 1 – 7 vol.%. One of them (RD78) was stopped after ten minutes because of a clogged feed gas system. The growth rates displayed in Fig. 4.11 show no clear correlation to the  $CH_4$  flow rates. In general, the already observed influence of the temperature gradient within the furnace is detected again. Only RD68 shows a different growth behavior with low growth rates at the levels L2-L4 and comparable high growth rate at level L1.



Fig. 4.11: Coating growth rates of undoped  $AI_2O_3$  coatings with different amount of  $CH_4$  gas: 1 l/h (RD67), 3 l/h (RD77), 5 l/h (RD68), 7 l/h (RD79). Gas flow direction from right to left.

#### 4.3.2 Crystal structure

The predominating Al<sub>2</sub>O<sub>3</sub> modification observed for coatings grown with additional methane was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Only in RD79, a significant amount of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> phase and traces of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> were detected. The deposition runs with lower CH<sub>4</sub> flow rates (RD67, RD77) show main peaks of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and traces of the  $\kappa$ -phase marked by parentheses.

Tab. 4.4:  $AI_2O_3$  modifications formed on C substrates with additional CH<sub>4</sub> gas and H<sub>2</sub> carrier gas: 1 I/h (RD67), 3 I/h (RD77), 5 I/h (RD68), 7 I/h (RD79). Low phase contents are marked by parenthesis.

	Comment	С
RD67	1 l/h CH <sub>4</sub>	α+(κ)
RD77	3 l/h CH <sub>4</sub>	α+(κ)
RD68	5 l/h CH <sub>4</sub>	α
RD79	7 l/h CH <sub>4</sub>	$\kappa + \alpha + (\theta)$

#### 4.3.3 Coating morphology

The morphology investigations show different grain sizes without clear dependency according to the different methane gas flows (Fig. 4.12). RD67 and RD68 exhibit coarser grains compared to the  $H_2$  reference RD47 whereas RD77 and RD79 show no significant differences.



Fig. 4.12: SEM surface structure of undoped  $AI_2O_3$  coatings grown with additional  $CH_4$  gas: 1 l/h (RD67), 3 l/h (RD77), 5 l/h (RD68), 7 l/h (RD79).

## 4.4 Aluminium strontium oxide

Three experiments concerning Sr-doping were performed in standard carrier gas mixture (RD57), H<sub>2</sub> carrier gas (RD58) and with additional NH<sub>3</sub> (RD65). As mentioned above, the SrCl<sub>2</sub> is placed in the Mo-reactor within the Reetz furnace.

## 4.4.1 Coating growth rate

Fig. 4.13 clearly presents the increased coating growth rate when only  $H_2$  as carrier gas is used (RD58) compared to the standard carrier gas (RD57). The additional NH<sub>3</sub> (RD65) causes an increasing growth rate on those samples close to the gas inlet, where deposition temperatures are lower. This results in a continuous decline of the growth rate from level L4 to level L1, attributed to a depletion of the reactants.



Fig. 4.13: Coating growth rates of Sr-doped  $AI_2O_3$  produced in different gas atmospheres standard gas composition (RD57),  $H_2$  carrier gas (RD58), additional NH<sub>3</sub> (RD65). Gas flow direction from right to left.

#### 4.4.2 Chemical composition

The doping element Sr was qualitatively detected by GDOES on all the deposition runs of the Sr doped  $Al_2O_3$  coating. The Sr concentration depth profile of RD57 (Fig. 4.14a) shows an almost constant Sr distribution within the  $Al_2O_3$  coating except at the vicinity of the coating surface. In deposition run RD58, a high Sr-peak at the  $Al_2O_3$ /TiCN interface could be observed which can be explained by evaporation of SrCl<sub>2</sub> during the heating period. The lower rise of the Sr-amount at the coating surface displayed in Fig. 4.14b can be explained by a higher evaporation rate of Sr due to the higher hydrogen amount in RD58 and a subsequent depletion of the SrCl<sub>2</sub> in the reactor. The deposition run with additional NH<sub>3</sub> (RD65, Fig. 4.14c) leads to an increasing nitrogen amount in the outermost layer, which is similar to the observation in chapter 4.2.2.



Fig. 4.14: GDOES plots of Sr doped Al<sub>2</sub>O<sub>3</sub> coatings on C substrates.

#### 4.4.3 Crystal structure

The structure of Sr-doped  $AI_2O_3$  coatings (Tab. 4.5) is dominated by  $\alpha$ - $AI_2O_3$ . Especially on substrate C, only  $\alpha$ -peaks were detected. Other substrates exhibited frequently small amounts of  $\kappa$ - $AI_2O_3$  marked by parentheses. Ammonia addition (RD65) causes an amorphous phase, where the GAXRD pattern shows only substrate and precoating peaks.

Tab. 4.5:  $AI_2O_3$  modifications of Sr doped  $AI_2O_3$  depending on substrate material. Low phase contents are marked by parenthesis.

	Comment	А	В	С	Мо
RD57	standard	α+(κ)	α+(κ)	α	α
RD58	H <sub>2</sub>	α	α	α	α+(κ)
RD65	standard + NH <sub>3</sub>	-	_	amorphous	-

## 4.4.4 Coating morphology

The deposition run with additional Sr performed with the standard carrier gas mixture (RD57, Fig. 4.15a) shows no significant differences compared to the reference (RD48, Fig. 4.4a), while the H<sub>2</sub> run RD58 (Fig. 4.15b) shows a slightly coarser grain structure compared to the related reference (RD47, Fig. 4.5a). The coating deposited with additional NH<sub>3</sub> (RD65, Fig. 4.15c) seems to be rather fine structured but rough at the same time. However, charging effects cause a blurred image which makes the interpretation difficult.



Fig. 4.15: SEM surface structure of Sr-doped  $AI_2O_3$  coatings produced in different gas atmospheres: a) standard gas composition, b)  $H_2$ , c) additional  $NH_3$ .

## 4.5 Aluminium yttrium oxide

Similar to Sr, Y-doping of  $AI_2O_3$  was investigated with the standard carrier gas mixture (RD55),  $H_2$  carrier gas (RD56) and with additional NH<sub>3</sub>. For the latter, two deposition runs with different temperature gradients (RD64, RD66) were performed. It should be noted that also YCI<sub>3</sub> may be evaporated due to the experimental alignment during the heating process and deposited on the substrate surface, as observed for Sr-deposition (see chapter 4.4.2).

## 4.5.1 Coating growth rate

The coating growth rate shows a clear trend with regard to the different gas atmospheres (see Fig. 4.16). The deposition run RD55 (standard carrier gas) shows the lowest deposition rate while the  $H_2$  carrier gas (RD56) causes slightly faster growth with nearly constant coating thickness on all levels. Further increased growth rates are observed with additional NH<sub>3</sub> at lower deposition temperatures compared to RD55 and RD56; however, the reason for the highest growth rate at the lowest deposition temperature is yet unknown. The lower growth rate for RD64 at level L1 can be explained by a depletion of precursor gases due to the high deposition rates

at level L2 and L3. A similar effect was observed for the Sr-doped run RD65 (see chapter 4.4.1).



Fig. 4.16: Coating growth rates of Y-doped  $Al_2O_3$  using different gas atmospheres ( $T_R$  = reactor temperature). Gas flow direction from right to left.

#### 4.5.2 Chemical composition

Only small amounts of Y could be detected by GDOES whereas the highest amount segregates close to the coating surface (Fig. 4.17).



Fig. 4.17: GDOES plot of Y-doped  $Al_2O_3$  on C.

Small oscillations of Y concentration are visible within the  $AI_2O_3$  layer and a small Y peak occurs also at the  $AI_2O_3$ /TiCNO interface. The concentration depth-profile of Y is similar for C- and Mo-substrates. For deposition runs with additional  $NH_3$  (RD64, RD66) an increasing N-amount within the outermost layer could be observed

which is also detected for the  $NH_3$  addition experiments with Sr (RD65, cf. chapter 4.4.2) and without doping elements (RD60, cf. chapter 4.2.2).

#### 4.5.3 Crystal structure

Considering A-, B- and C-substrates, the predominant  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure can be observed with traces of  $\kappa$ - and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (distinguished by round parentheses) when using the standard gas mixture, while  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is the predominant phase when using H<sub>2</sub> carrier gas. However, on Mo-substrates the opposite trend is visible, but  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is dominant in both cases.

The additional  $NH_3$  in RD64 and RD66 cause an amorphous outermost layer, where the GAXRD patterns only show substrate and precoating peaks.

Tab. 4.6:  $AI_2O_3$  modifications of Y-doped  $AI_2O_3$  on different precoatings and substrates. Low phase contents are marked by parenthesis.

	Comment	А	В	С	Мо
RD55	standard	$\alpha$ +( $\kappa$ + $\theta$ )	α+(κ+θ)	α+(κ+θ)	<b>κ</b> +(θ)
RD56	H <sub>2</sub> only	$\alpha + \kappa + (\theta)$	$\kappa + (\alpha + \theta)$	$\kappa + (\alpha + \theta)$	$\kappa + (\alpha + \theta)$
RD64	standard + $NH_3$	_	_	amorphous	-
RD66	standard + $NH_3$	_	_	amorphous	-

## 4.5.4 Coating morphology

The Y-doped  $AI_2O_3$  coating deposited with  $H_2$  carrier gas (R56) shows a larger grain size (Fig. 4.18b) compared the related reference coating (RD47, see Fig. 4.5a), while the grain size of Y-doped (Fig. 4.18a) and undoped  $AI_2O_3$  (see Fig. 4.4a) is similar for coatings deposited with standard gas mixture. The additional NH<sub>3</sub> causes a blurred image (Fig. 4.18c) due to charging effects which are similar to the Sr-doping (Fig. 4.15c).



Fig. 4.18: SEM surface structure of Y-doped  $AI_2O_3$  produced in different gas atmospheres: a) standard gas composition b)  $H_2$  only, c) additional  $NH_3$ .

## 4.6 Aluminium manganese oxide

Four coating experiments (one with standard carrier gas mixture and three with  $H_2$  carrier gas) with additional MnCl<sub>2</sub> were performed in different experimental configurations as described in chapter 3.1.1, but MnCl<sub>2</sub> was only detected by GDOES for RD83 (H<sub>2</sub> only, MnCl<sub>2</sub> placed on top of the graphite tube, see Fig. 3.3). As visible in Fig. 4.19, a higher amount of Mn could be detected close to the surface but no pink or red coating color was observed, which indicates a much lower incorporated amount of Mn compared to literature [37].



Fig. 4.19: GDOES plot of Mn-doped Al<sub>2</sub>O<sub>3</sub> on C.

In correlation to the chemical composition, only the SEM micrographs of RD83 shows differences compared to the H<sub>2</sub> reference RD47. The additional Mn in the Al<sub>2</sub>O<sub>3</sub> coating causes the finest morphology within this work, hence Mn-doping represents a very promising approach from the application point of view (Fig. 4.20a). Furthermore, this grain refining influence of manganese seems not to be reported in literature so far. Despite the fine grained structure, the expected hardness increase was not observed. The cross-section image in Fig. 4.20b shows a layer thickness of about 6  $\mu$ m, i.e. the coating growth rate increases by 25% compared to the reference RD47. Assuming a proportional correlation of coating thickness and grain size [7], the grain refinement effect would be still more pronounced for Mn-doped coating with a coating thickness similar to the reference RD47.



Fig. 4.20: (a) SEM surface structure (b) and fracture cross-section of Mn-doped  $AI_2O_3$  produced in  $H_2$  only.

Many different modifications of  $Al_2O_3$  could be detected for the first Mn experiments (RD73, RD74, RD76) while only  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is present for the Mn containing Al<sub>2</sub>O<sub>3</sub> coating (RD83). Hence, the incorporation of detectable amounts of Mn stabilizes the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> modification.

	Comment	С
RD73	standard / $T_{MnCl2}$ = 600 °C	α+(γ+δ+η)
RD74	H₂ / T <sub>MnCl2</sub> = 600 ℃	α+(κ+θ)
RD76	H₂ / T <sub>MnCl2</sub> = 650 ℃	$\alpha + \kappa$
RD83	$H_2$ / $T_{MnCl2}$ = 700 °C (L05)	α

Tab. 4.7:  $AI_2O_3$  modifications of Mn-doped  $AI_2O_3$ . Low phase contents are marked by parenthesis.

## 4.7 Aluminium niobium oxide

Three experiments were performed with standard gas mixture and two more were carried out with  $H_2$  gas composition. NbCl<sub>5</sub> was volatilized using two different experimental configurations but within the  $Al_2O_3$  coating no Nb was detected with GDOES, EDX and WDX. Only for the deposition run RD85, a change in film morphology was observed on the Mo substrate, where coarse plate-like grains are visible (Fig. 4.21b). For the same deposition run, coating morphology changes just slightly on substrates C (Fig. 4.21a) compared to RD47 (Fig. 4.5a).



Fig. 4.21: SEM surface structure of Nb-doped  $AI_2O_3$  on different substrates.

## 4.8 Aluminium tantalum oxide

The two experiments within the Ta-system were carried out with standard gas mixture (RD59) and H<sub>2</sub> carrier gas (RD61) in a second reactor alignment. No Ta was detected by GDOES or EDX. A coarser coating morphology was observed on C-substrates (Fig. 4.22a) compared to RD47 (H<sub>2</sub> reference, see Fig. 4.5a) while on the Mo substrate very large grains embedded in a needle base structure are seen (Fig. 4.22b).



Fig. 4.22: SEM surface structure of Ta-doped Al<sub>2</sub>O<sub>3</sub> on different substrates.

## 4.9 Aluminium silicon oxide

The eight experiments with H<sub>2</sub> carrier gas and additional SiCl<sub>2</sub> were performed with two different experimental setups, as mentioned in chapter 3.1.2. The deposition runs RD69-RD72 were performed with a second reactor, where the consumption of SiCl<sub>4</sub> could not be controlled in-situ. Consequently, in deposition runs RD70 and RD71, the SiCl<sub>4</sub> was completely evaporated during deposition and the coating process was finished without doping element. For deposition runs RD69 and RD75, the evaporated SiCl<sub>4</sub> was transported with a gas lance ( $\emptyset$ 1.5 mm) through the Mo-reactor into the furnace. This led to clogging troubles during the coating process,

where e.g. run RD75 had to be stopped after 145 minutes. The experiments RD75, RD81, RD82 and RD84 were carried out with a glass bubbler, in order to investigate the evaporation rate depending on different H<sub>2</sub> flow rates through the liquid SiCl<sub>4</sub> as can be seen in Fig. 4.23a. The ascertained evaporation rates, shown in Fig. 4.23b, were compared to the theoretical values which were calculated according to Eq. 4.2 [64] where  $p_{SiCl4}$  is the vapor pressure of SiCl<sub>4</sub> and  $p_{atm}$  the atmospheric pressure. The plot shows a linear dependency between evaporation rate and H<sub>2</sub> flow rate and an almost perfect agreement between the calculated and experimentally investigated values. Two runs, RD72 and RD84, were performed with additional CH<sub>4</sub> and NH<sub>3</sub>, respectively.



Fig. 4.23: (a) Evaporation rates of SiCl<sub>4</sub> in dependency of different H<sub>2</sub> flow rates through the bubbler (b) Comparison of experimental and theoretical evaporation rates.

#### 4.9.1 Coating growth rate

All deposition runs with additional SiCl<sub>4</sub> (H<sub>2</sub> carrier gas) show generally a significantly increased growth rate compared to the reference RD47 (see Fig. 4.24). The highest growth rate on level L1 (highest deposition temperature) was observed for RD72 where also CH<sub>4</sub> was added. In general, a tendency of increasing coating thickness for level L4 to L1 is visible. Only the experiments with the highest growth rates at level L4 to L2 (RD82, RD84) show a decreasing growth at level L1 which is attributed to a depletion of precursor gases caused by the former fast growth. Different experimental configurations, e.g. an additional lance in the deposition runs RD69 and



RD75, influenced the coating growth and process stability. Hence, a clear correlation of H<sub>2</sub> flow via SiCl<sub>4</sub> bubbler and growth rate is not possible for all experiments.

Fig. 4.24: Coating growth rates of Si-doped  $Al_2O_3$  with different  $H_2$  flow rates through the bubbler. Gas flow direction from right to left.

#### 4.9.2 Chemical composition

Si could be quantitatively detected by EDX (Tab. 4.8) and qualitatively detected by GDOES (Fig. 4.25).

	H <sub>2</sub> - Bubbler [l/h]	additional gas [l/h]	Si [at%]
RD84	1.5	1 NH <sub>3</sub>	14.72
RD69	2	-	0
RD82	3	-	20.17
RD72	5	5 CH <sub>4</sub>	19.74
RD75	5	-	15.93
RD81	8	-	17.94
RD71	12	-	12.38
RD70	35	-	1.9

Tab. 4.8 : EDX analysis of silicon in dependence of different  $H_2$ -flow rates through the SiCl<sub>4</sub> bubbler.



Fig. 4.25: GDOES plots of Si-doped Al<sub>2</sub>O<sub>3</sub> films on C substrates produced with different H<sub>2</sub>-flow rates through the SiCl<sub>4</sub> bubbler, indicated by the number in brackets.

For deposition run RD69, Si was only detected by GDOES where a small but constant Si concentration within the Al<sub>2</sub>O<sub>3</sub> coating is visible in the depth profile. The deposition runs RD70 and RD71 in Fig. 4.25c-d show a decreasing amount of Si close to the coating surface, which results from the complete evaporation of SiCl<sub>4</sub> during deposition, as already mentioned. This fact is also reflected in the rather surface sensitive EDX analysis in Tab. 4.8, i.e. both coatings show a lower Si-content due to an outermost layer of Al<sub>2</sub>O<sub>3</sub> deposited after the SiCl<sub>4</sub> had been consumed completely. The highest coating thickness could be observed for the deposition run RD72 (additional CH<sub>4</sub>), and a very high content of Si was investigated for RD72 and RD82 by EDX (~20 at.%, see Tab. 4.8) and GDOES (see Fig. 4.25e, g). Contrary, deposition run RD75 shows the lowest coating thickness and decreasing Si content close to the coating surface which was caused by process instabilities (clogging, Fig. 4.25f). The elongated surface structures (see Fig. 4.26f) contain a relatively high Si amount of ~30 at.%. A lower H<sub>2</sub> flow rate of 1.5 l/h through the SiCl<sub>4</sub>-bubbler in combination with additional  $NH_3$  (RD84) leads to lower Si content (~15 at.%) compared to the maximum Si content in RD82 measured by EDX. The still high Si amount is also documented in the GDOES plot (Fig. 4.25h). Due to cracking and chipping of the coating, GDOES was not possible for deposition run RD81.

### 4.9.3 Crystal structure

Many different modifications of Si-doped  $Al_2O_3$  were detected with XRD, which are listed in Tab. 4.9. The amorphous phase on RD72, RD81 and RD82 could be related to the high coating growth rate and consequently insufficient time for crystal growth similar to NH<sub>3</sub> experiments as well as the tendency of SiO<sub>2</sub> to form an amorphous phase [65, 66]. The low Si concentration of RD69 agrees well with the crystal structure which is similar to the reference RD47 where also  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the predominant phase. After the complete evaporation of SiCl<sub>4</sub> in RD70, a predominant  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> and Al-Si-O phase (according to JCPDS # 01-082-1237) with small amounts of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were detected. A slower but also complete evaporation of SiCl<sub>4</sub> in RD71 leads to a shorter deposition time without SiCl<sub>4</sub> and consequently no crystalline Al<sub>2</sub>O<sub>3</sub> is detected. The crystal structure of RD75, where clogging occurred during the final deposition phase, exhibits an  $\alpha$ - Al<sub>2</sub>O<sub>3</sub>,  $\kappa$ '- Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> phase. With regard to deposition run RD70, RD71 and RD84 it seems that the amorphous

phase is first transferred into an Al-Si-O-phase and then into a crystalline  $Al_2O_3$  modification. Furthermore, the detected SiO<sub>2</sub> phase in RD70, RD75 and RD84 may also form a mullite phase together with  $Al_2O_3$ .

	H <sub>2</sub> - Bubbler [l/h]	Bubbler [l/h] Si [at%] additional gas [l/h]		С
RD84	1.5	14.72	1 NH <sub>3</sub>	$\alpha$ +(Al-Si-O-phase+SiO <sub>2</sub> )
RD69	2	0	-	$\alpha$ +( $\kappa$ + $\theta$ )
RD82	3	20.17	-	amorphous
RD72	5	19.74	5 CH <sub>4</sub>	amorphous
RD75	5	15.93	-	$\alpha$ + $\kappa$ '+SiO <sub>2</sub>
RD81	8	17.94	-	amorphous
RD71	12	12.38	-	amorphous+Al-Si-O-phase
RD70	35	1.9	-	$\kappa \text{+AI-Si-O-phase} \text{+} (\alpha \text{+SiO}_2)$

Tab. 4.9: Al<sub>2</sub>O<sub>3</sub> modifications of Si-doped Al<sub>2</sub>O<sub>3</sub>. Low phase content are marked by parenthesis.

#### 4.9.4 Coating morphology

The SEM micrographs of RD69 and RD70 (Fig. 4.26b-c) show a slightly coarser grain structure compared to the H<sub>2</sub> reference RD47 (Fig. 4.26a) which may result from their higher coating thickness. Otherwise the morphology of RD69 is very similar to RD47 which may be explained by the low Si content in the coating. For the deposition run RD71 and RD72 (Fig. 4.26d-e), a very fine grained structure can be observed. The morphology of the deposition run RD75 (Fig. 4.26f) with additional CH<sub>4</sub> gas, which was stopped after 145 minutes, shows spherical and elongated surface structures with a high Si content (~30 at.%). A coating morphology without crystal facets but large grains is observed on RD81 and RD82 (Fig. 4.26g-h). The additional NH<sub>3</sub> causes a finer morphology for RD84 (Fig. 4.26i) which could only be displayed with a diffuse SEM picture.

In order to characterize the coating morphology in detail, fracture cross-section images were performed for selected Si-doped samples. The micrograph in Fig. 4.27a displays deposition run RD47 on C-substrate, while the Si-doped coatings of RD69 (Fig. 4.27b) and RD72 (Fig. 4.27c) are shown on A-substrates.

The fracture cross-section of RD69 (Fig. 4.27b) illustrates similar coating thickness but a slightly rougher surface compared to RD47 (Fig. 4.27a). The highest coating thickness within this work was observed for deposition run RD72 (Fig. 4.27c).



Fig. 4.26: SEM surface structure of silicon doped Al<sub>2</sub>O<sub>3</sub>.



Fig. 4.27: SEM fracture cross-sections of undoped  $Al_2O_3$  on C-substrate and silicon doped  $Al_2O_3$  with TiCN/TiN precoating (A-substrate).

## 4.10 Comparison of different doping elements

## 4.10.1 Growth rate

A comparison of undoped  $Al_2O_3$  films deposited with different carrier gas mixtures (Fig. 4.28) shows a higher growth rate for  $H_2$  carrier gas (RD47) compared to the standard carrier gas mixture (RD48). With additional NH<sub>3</sub> (RD60) the growth rate further increases although the deposition temperature is ~350 °C lower compared to RD47 and RD48. The reasons for these effects may be a higher decomposition rate of AlCl<sub>3</sub> and a faster desorption of the reaction products from the substrate surface due to the higher H<sub>2</sub> amount (cf. chapter 2.2.3). Furthermore, with the introduction of NH<sub>3</sub>, highly reactive hydrogen and nitrogen species appear which could expedite the deposition process, similar to H<sub>2</sub> addition only, but also allow the formation of additional nitride or oxynitride phases within the coating.



Fig. 4.28: Comparison of the coating growth rates of deposition runs RD47 (H<sub>2</sub> only, T<sub>dep</sub> = 1050 °C), RD48 (standard gas, T<sub>dep</sub> = 1050 °C) and RD60 (standard gas + NH<sub>3</sub>, T<sub>dep</sub> = 700 °C). Gas flow direction from right to left.

The influence of doping elements on the growth rate of coatings deposited with standard carrier gas mixture and  $H_2$  carrier gas is displayed in Fig. 4.29a-b, respectively. The additional dopants have a growth reducing effect with the standard carrier gas, compared to the reference RD48. On the other hand, Ta- and Mn- doping increase the growth rate for the experiment with  $H_2$  carrier gas, while Sr-, Nb- and Y-doping does not cause significant changes compared to the reference.



Fig. 4.29: Comparison of the influence of doping elements on the growth rate in (a) standard gas and (b) H<sub>2</sub> only. Gas flow direction from right to left.

#### 4.10.2 Coating hardness

For the investigated carrier gas mixtures, the coating RD47 ( $H_2$  carrier gas) shows the highest hardness value with 15.1 GPa (Fig. 4.30). The coating hardness for the deposition runs RD46 with mainly N<sub>2</sub> and RD63 with mainly Ar are similar to RD48 (standard carrier gas) within the range of 12 to 13 GPa, while RD45 with more H<sub>2</sub> corresponding to RD48 is slightly softer. CH<sub>4</sub> gas addition, above 3 l/h, generally increases the hardness. There, the coating RD77 show the highest hardness value within this work (18.5 GPa).



Fig. 4.30: Influence of carrier gas variations (left hand side) and additional  $CH_4$  (right hand side) on the hardness of  $AI_2O_3$  coatings.

Compared to the respective reference runs, similar coating hardness was measured for Nb (RD53, RD54), Sr (RD57, RD58) and Mn (RD74, RD83), while Mn shows an increased hardness value when using standard gas atmosphere (RD73) as presented in Fig. 4.31. One Nb-doped (RD85) and one Mn-doped (RD76) coating were considerably softer than the references, while Y-doping generally causes lower hardness values. Within this figure, red symbols refer to deposition experiments with "H<sub>2</sub> carrier gas" and green symbols refer to experiments with standard gas composition. The dashed red line represents the H<sub>2</sub> reference run (RD47) while the dashed green line represents the standard reference (RD48).



Fig. 4.31: Influence of the doping elements (Nb, Y, Sr, Ta, Mn) on the hardness of Al<sub>2</sub>O<sub>3</sub> coatings, compared to RD47 (dash-dotted red line) and RD48 (dashed green line). H<sub>2</sub> carrier gas and standard carrier gas mixture are indicated by red and green symbols, respectively.

Due to the extensive investigation of Si-doping, the hardness of these deposition runs are displayed separately in Fig. 4.32. Compared to the H<sub>2</sub> reference run RD47, the Si-doped Al<sub>2</sub>O<sub>3</sub> coatings show a decreasing coating hardness. The presence of SiO<sub>2</sub> with a comparatively low hardness ranging from 8 to 9 GPa [67, 68], which is still lower for porous SiO<sub>2</sub> films [69], as well as higher coating thickness and coarser grains could be responsible for the softer coating. The lowest hardness value was observed for RD72 with the highest coating thickness (35 µm) deposited with additional CH<sub>4</sub>. With regard to the coating hardness at low SiCl<sub>4</sub> addition, even higher values might be possible at very low SiCl<sub>4</sub> flow rates. As such low flow rates could not be realized with the experimental setup of the Reetz furnace, future upscaling experiments are needed to investigate them.



Fig. 4.32: Influence of Si doping and different  $H_2$  flow rates through the SiCl<sub>4</sub> bubbler (which controls the SiCl<sub>4</sub> evaporation) on the hardness of Al<sub>2</sub>O<sub>3</sub> coatings, H<sub>2</sub> reference is indicated by a red symbol.

#### 4.10.3 Textures

The coating texture was evaluated by calculating the texture coefficients (TC) of the eight most intensive  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> peaks (JCPDS file # 00-010-0173). In order to investigate the influence of the different gas variations on the texture, TC's were calculated for the deposition runs RD45-RD48 on different substrate materials (Tab. 4.10). Low (<0.4), medium (1.2 - 1.6) and high (>1.6) TC's are highlighted with yellow, orange and red shaded cells, respectively. On all substrates a slightly increased (110) texture was observed for increasing H<sub>2</sub> amount (RD45 and RD47). Independent the carrier gas variation, the most pronounced orientation was (214). In general the texture is mainly influenced by different substrate materials, e.g. a high (214) texture coefficient was obtained for C substrates, which is less pronounced on B-, A- and Mo-substrates.

Tab. 4.10: Texture coefficients of undoped Al2O3 coatings grown with different gas compositions: RD45 (standard + more H2), RD46 (mainly H2), RD47 (H2 only), RD48 (standard gas). Low (<0.4), medium (1.2 - 1.6) and high (>1.6) TC's are highlighted with yellow, orange and red shaded cells.

				С			E	В			1	А			Мо		
2theta	h	k		RD45	RD46	RD47	RD48	RD45	RD46	RD47	RD48	RD45	RD46	RD47	RD48	RD47	RD48
25.58	0	1	2	0.3	0.19	0.21	0.31	0.64	0.71	0.42	0.54	0.75	0.78	0.35	0.78	0.7	0.89
35.14	1	0	4	0.21	1.17	0.31	1.16	0.96	1.21	0.73	1.26	0.76	1.41	1.05	1.78	1.16	1.13
37.79	1	1	0	1.85	1.24	1.67	1.02	1.38	1.14	1.62	1.1	1.34	0.79	1.46	0.49	1.12	1.06
43.36	1	1	3	0.55	0.57	0.56	0.51	1.1	0.98	1.16	0.98	1.07	1.05	1.17	1.04	1.08	0.98
52.55	0	2	4	1.35	1.06	1.21	1.22	0.98	0.99	0.91	1.01	0.94	1	0.81	0.94	0.9	0.99
57.52	1	1	6	0.26	0.71	0.29	0.83	0.81	0.93	0.71	0.96	0.86	1.08	0.78	1.25	1.01	0.94
66.55	2	1	4	3.04	2.78	3.45	2.59	1.36	1.37	1.54	1.54	1.17	1.06	1.46	1.1	1.06	1.12
68.20	3	0	0	0.43	0.26	0.31	0.35	0.77	0.68	0.89	0.62	1.11	0.81	0.92	0.63	0.97	0.89

The texture of  $AI_2O_3$  can be influenced by the addition of doping elements. Tab. 4.11 shows the influence of Y-doping using standard gas (RD55) and H<sub>2</sub> only (RD56). Sr-doping (RD57), Si-doping (RD69) and Mn-doping experiments (RD83) are displayed only for deposition runs with H<sub>2</sub> carrier gas. A lower TC's for the (214) orientation can be observed on the C-substrate for the deposition run with only H<sub>2</sub> (RD56). This observation is contrary to the undoped experiments RD47 (only H<sub>2</sub>) and RD48 (standard gas). Another example for the influence of doping is Si (RD69) on C-substrates, where a pronounced (104) texture is visible.

Nevertheless, the textures seem to be strongly influenced by the type of substrates, although doping causes significant changes.

Tab. 4.11: Texture coefficients of Y-,Sr-, Si- and Mn-doped  $AI_2O_3$ , calculated for the  $\alpha$ - $AI_2O_3$  phase fraction. Low (<0.4), medium (1.2 - 1.6) and high (>1.6) TC's are highlighted with yellow, orange and red shaded cells, respectively.

l				С					В		А		Мо
2theta	h	k	Τ	RD55	RD56	RD57	RD69	RD83	RD55	RD56	RD55	RD56	RD56
25.58	0	1	2	0.28	0.69	0.27	0.4	0.23	0.74	0.79	0.85	0.77	0.52
35.14	1	0	4	0.25	1.11	0.82	1.32	0.09	0.58	1.1	1.03	1.44	1.13
37.79	1	1	0	2.01	1.07	1.47	1.22	2.34	1.67	1.07	1.08	0.92	1.39
43.36	1	1	3	0.58	0.91	0.55	1.03	0.66	1.02	1.04	1.09	0.91	0.62
52.55	0	2	4	1.38	1.16	1.32	0.9	1.02	0.98	1.04	0.96	0.95	1.31
57.52	1	1	6	0.2	0.92	0.48	0.89	0.21	0.65	0.8	0.88	1.24	0.72
66.55	2	1	4	2.77	1.52	2.75	1.56	2.71	1.46	1.42	1.22	1	1.64
68.20	3	0	0	0.53	0.62	0.34	0.67	0.74	0.9	0.75	0.89	0.76	0.66

## 4.10.4 Oxidation protection

For the investigation of the oxidation behavior of  $Al_2O_3$ -coatings, mainly doped coatings on Mo were tested in air, for 12 hours at 550 °C, for 24 hours at 650 °C and for 24 hours at 750 °C. The samples w ere weighted after each test and the weight measurements were in a good agreement with the optical observations, as exemplarily shown in Fig. 4.33. After 12 hours at 550 °C, no mentionable oxidation effect could be observed while after 24 hours at 750 °C all the Mo samples were completely oxidized. A rather good oxidation protection could be observed for RD68, RD69 and RD70 while RD66 and RD67 show an insufficient oxidation protection (Fig. 4.33a). This is also confirmed by the higher mass loss of RD66 and RD67 displayed in Fig. 4.33b. No clear correlation between doping and oxidation behavior could be observed, e.g. Si-doping and CH<sub>4</sub> addition yields a good performance on selected samples while the same doping elements shows bad oxidation properties on others.

	RD65	RD67	RD69			
,	/	/	/		Doping element	mass loss [mg]
	1			RD65	Sr	64.3
1 des				RD66	Y	349.2
				RD67	$CH_4$	964
12 C				RD68	CH <sub>4</sub>	3.5
LAS	1			RD69	Si	3.9
				RD70	Si	166.2
	RD66	RD68	RD70	ſ		
	â	a)			b)	

Fig. 4.33: a) Mo substrates coated with doped  $Al_2O_3$  after 24h oxidation at 650 °C in air b) Mass loss after oxidation.

# 5 Summary

The goal of this thesis was to affect the microstructure, texture, hardness and oxidation behavior of  $Al_2O_3$  coatings by additional doping elements and gas mixture variations. Therefore, chlorides of Nb, Ta, Sr, Y, Si and Mn were evaporated and co-deposited with  $Al_2O_3$ . Furthermore, the influence of NH<sub>3</sub> and CH<sub>4</sub> addition, different substrate materials and deposition temperatures between 700 and 1050 °C were investigated.

The coatings were produced in a vertical CVD hot wall reactor (laboratory-scale) with three separate controllable molybdenum heating coils. The precursor and carrier gas mixture flowed top down and a coating was deposited in the lowest hottest zone. Depending on the melting temperature of the chlorides, a second reactor was used for their evaporation. Alternatively, the dopant chloride was evaporated in the Al-chlorination reactor (single-reactor configuration), which was placed within the topmost heating zone showing the lowest temperature.

Based on an undoped  $AI_2O_3$  coating deposited with a standard gas composition  $(H_2/Ar/N_2, reference)$  different carrier gas mixtures were examined at 1050 °C deposition temperature. A higher coating growth rate and a higher coating hardness (~15 GPa) could be observed for a carrier gas consisting of H<sub>2</sub> only. Furthermore, the film grown with the H<sub>2</sub> carrier gas shows a slightly coarser grain structure compared to the reference. The addition of NH<sub>3</sub> causes an even faster coating growth, which is also pronounced at low deposition temperatures (700 °C). Consequently, insufficient time for crystal growth as well as nitrogen incorporation leads to an amorphous structure.

Additional CH<sub>4</sub> causes a comparable coarser grain but yields also to the highest hardness value of all deposition runs (~18.5 GPa).

The experiments with Y- and Sr-doping were performed using the single-reactor configuration with standard carrier gas, H<sub>2</sub> carrier gas and NH<sub>3</sub> addition. In all cases, the respective dopant was incorporated in the Al<sub>2</sub>O<sub>3</sub> coating and leads to coarser grain size with H<sub>2</sub> carrier gas. Moreover, Sr stabilizes the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase and decreases the growth rate of Al<sub>2</sub>O<sub>3</sub> deposited with standard and H<sub>2</sub> carrier gas.

Experiments with Mn-doping were also conducted in single-reactor configuration with standard and  $H_2$  carrier gas composition. The doping element could be only detected in the particular coating grown with  $H_2$  carrier gas at higher evaporation temperature, where the Mn-precursor was placed in the second heating zone. For this experiment,

the Mn incorporated in the  $AI_2O_3$  coating causes the finest structure of all performed experiments and higher growth rates, but showed a hardness value comparable to the reference. For another Mn-doped  $AI_2O_3$  coating deposited with standard gas, a raised hardness value (16.9 GPa) compared to the reference (12.4 GPa) could be observed.

Deposition experiments with the NbCl<sub>5</sub> and TaCl<sub>5</sub> were carried out with a second reactor using standard and H<sub>2</sub> carrier gas. It was not possible to incorporate detectable amounts of Nb or Ta into the Al<sub>2</sub>O<sub>3</sub> coating, most likely due to an insufficient heating of the connection line between both reactors. Consequently, clogging of the feed line occurred, which impeded precursor transport. Nevertheless, for H<sub>2</sub> carrier gas, Nb-doping resulted in formation of an acicular structure mixed with coarse grains and Ta-doping causes very large grains embedded in a needle-shaped matrix. Furthermore, Ta-doped Al<sub>2</sub>O<sub>3</sub> coatings deposited with H<sub>2</sub> carrier gas show an increased growth rate.

For the investigations with SiCl<sub>4</sub> precursor and its carrier gas, the dependency of SiCl<sub>4</sub> evaporation and different H<sub>2</sub> flow-rates through the SiCl<sub>4</sub>-bubbler are in good agreement with basic estimations. In general, Si-doping increases coating growth rates compared to the reference run, where a combination of SiCl<sub>4</sub> and CH<sub>4</sub> causes the highest growth rates of all experiments (11.7 µm/h). A rougher surface and coarser grains could be observed for small but constant Si concentration depth profile. The highest Si-content in the Al<sub>2</sub>O<sub>3</sub> coating was ~20 at.%, i.e. Si was the only dopant used in this thesis which could be incorporated with high concentration. The detected crystal structure of Si-doped Al<sub>2</sub>O<sub>3</sub> coatings includes  $\alpha$ -,  $\kappa$ - and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> as well as SiO<sub>2</sub>, Al-Si-O and an amorphous phase. The latter could be related to the fast coating growth and the consequently insufficient time for crystal growth as well as the tendency of SiO<sub>2</sub> to form an amorphous phase. It seems that a decreasing evaporation rate leads to a transformation of the amorphous phase first into an Al-Si-O-phase, and then into a crystalline  $Al_2O_3$  modification. Si-doped  $Al_2O_3$  coatings show decreasing hardness compared to the reference due to the softer SiO<sub>2</sub> and phases, higher coating thickness and coarser grains.

The texture of the  $AI_2O_3$  phase was influenced by all of the doping elements, where (110) and (214) are the most pronounced orientations. An increased texture coefficient can be observed especially for (110) by using  $H_2$  carrier gas. However, in general the texture is mainly influenced by the different substrates.

The oxidation behavior was investigated for doped  $AI_2O_3$  coatings deposited on Mo substrates. The test was performed for 12 hours at 550 °C, for 24 hours at 650 °C
and for 24 hours at 750 °C. For the lowest testing temperature no oxidation could be observed, while all samples were completely oxidized after the 750 °C test. CH<sub>4</sub>- and Si-doping improved the oxidation protection at 650 °C on selected samples, but no clear correlations between doping and oxidation behavior could be identified. One reason for the observation of different oxidation behavior may be an inhomogeneous coating thickness, e.g. in the vicinity of the contact points of substrate and sample holder.

Important know-how for upscailing and producing doped  $AI_2O_3$  coatings could be gained within this work, e.g. precursor handling, optimal gas atmosphere, optimal deposition temperature, controlling Si-incorporation, influence of the substrate on the  $AI_2O_3$  coating and the identification of beneficial and deteriorating doping effects.

Further investigations, performing up-scaling deposition experiments on a production plant would involve a more sophisticated gas flow control, e.g. a more precisely addition of low dopant amounts, as favorable for Si-doping. Moreover, the possibility of depositing alumina layer and base-layer with one run consequences a cleaner interface which is generally related to improved properties of the coating system.

## 6 Literature

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## 7 Symbols and abbreviations

$a_i$	Geometric constant
hkl	Miller indices
$G_{f-product}$	Gibbs free formation energy of products
$G_{f-reactantt}$	Gibbs free formation energy of reactants
G	Gibbs free Energy
Н	Enthalpy
n	Order of diffraction
р	Pressure
r*	Critical radius
Re	Reynolds' number
S	Entropy
S	Layer thickness
Т	Temperature
$T_b$	Boiling point
$T_m$	Melting point
$T_s$	Substrate temperature
$u_x$	Flow density
x	Distance from the inlet
γ	Surface energy
Δ	Layer thickness
$\Delta G_f$	Standard free energy change of formation
μ	Viscosity
ρ	Mass density
А	Constant
Ea	Activation energy
$\Delta G^*$	Free energy barrier
$\Delta G_{v}$	Chemical free energy per unit volume
N*	Nucleation rate
n <sub>s</sub>	Density of all possible nuclei sites
k	Boltzmann factor
Ι	Intensity
L	Level
ТС	Texture coefficient
T <sub>R</sub>	Reactor temperature

CVDChemical vapour depositionGBGrain boundaryGDOESGlow discharge optical emission spectroscopyISOInternational Standardizing OrganisationMCLMaterials Center LeobenPVDPhysical vapour depositionS40TCeratizit cemented carbide gradeSEMScanning electron microscopySNUNCutting insert geometry according to ISO 1832XRDX-ray diffractionLVDTLinear variable differential transformerRDSecondary electronSESack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	ASTM	American Society for Testing and Materials
GBGrain boundaryGDOESGlow discharge optical emission spectroscopyISOInternational Standardizing OrganisationMCLMaterials Center LeobenPVDPhysical vapour depositionS40TCeratizit cemented carbide gradeSEMScanning electron microscopySNUNCutting insert geometry according to ISO 1832XRDX-ray diffractionLVDTLinear variable differential transformerRDSecondary electronSESecondary electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	CVD	Chemical vapour deposition
GDOESGlow discharge optical emission spectroscopyISOInternational Standardizing OrganisationMCLMaterials Center LeobenPVDPhysical vapour depositionS40TCeratizit cemented carbide gradeSEMScanning electron microscopySNUNCutting insert geometry according to ISO 1832XRDX-ray diffractionLVDTLinear variable differential transformerRDSecondary electronSEBack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	GB	Grain boundary
ISOInternational Standardizing OrganisationMCLMaterials Center LeobenPVDPhysical vapour depositionS40TCeratizit cemented carbide gradeSEMScanning electron microscopySNUNCutting insert geometry according to ISO 1832XRDX-ray diffractionLVDTLinear variable differential transformerRDReetz depositionSESecondary electronBSEBack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	GDOES	Glow discharge optical emission spectroscopy
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RDReetz depositionSESecondary electronBSEBack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	LVDT	Linear variable differential transformer
SESecondary electronBSEBack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	RD	Reetz deposition
BSEBack scattered electronMXMixed modeEDXEnergy dispersive X-ray spectroscopy	SE	Secondary electron
MXMixed modeEDXEnergy dispersive X-ray spectroscopy	BSE	Back scattered electron
EDX Energy dispersive X-ray spectroscopy	MX	Mixed mode
	EDX	Energy dispersive X-ray spectroscopy

## 8 Appendix

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RD46	/5	200 × /±	430		1 75	(I/N] 111	2,1 4,	5 90,0	4,8	5,0	7,8				m, [g]	10,1392	10,1216	10,1644	10,1439	10,1172	9,9659	8,0305	52,9820		
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:	L t	470 A98	1050		2				1111						d <sub>m</sub> [mg]	10,84	16,16	39,47	75,1	70,17	54,42	58,61	4,6961		
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		470 680	1050		_										mv [g]	10,1256	10,1936	10,1522	10,1488	10,1025	10,0136	8,0538	60,7018	12.4±2.4	217±47
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222	2025 15 15	A70 497	1050	3	2		8	0							d <sub>m</sub> [mg]	1,7	1,8	2,4	3,2	2,8	2,9	4,5	3,2370		
	și.	>++	202			[%v] 100	0,0 4,1	0 53,4	4,3	13,4	0,0	10,	7 14,2		s [μm]	0,9	-	0,9	-						
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#	Donant	12	70	3 PE. PE.	time		total		CO <sub>2</sub> aft	ter5`on	±	ЧН	۵r. ۵.	Ē	level	L04	5	L02		L01 (~ P	os. 4)		cursor	н [Сма] + н	E [CMA] + E
		ī	1		[min]		flow	2	Ŭ Ľ	0 <sup>2</sup> H <sub>2</sub>		8	( 	13 (14	sample	A	A	A	A	в	υ	Mo	(in/out/loss)		r [aba] - r
Part Part P		UL P	01 007 0		1 75	[I/h]	110,1	4,5 6	50,0 4,	.,8 5,(	9' <u>7</u> ,8		16, 16,	0.	te : 21										
oranaara		4	200	3	2	[%v]	100,0	4,1 5	54,5 4,	44 44	2,17		0,9 14	5	s then!										
		170	AB0 10	50											mv [g]	10,1787	10,1977	10,1522	10,1346	10,0521	9,9596	8,0047	54,8667	13.7±2.2	242±32
RD53	NbCI <sub>2</sub>	s	3	432 156	175	[4/1]	110,3	4,5 ć	50,0 4	, 11 8,	0 2,0		12,0 16	3	m, [g]	10,1808	10,2012	10,157	10,1402	10,0581	9,967	8,01	50,0249		
	ì	tai 470	692 10	50		3									d <sub>m</sub> [mg]	2,1	3,5	4,8	5,6	6	7,4	5,3	4,8418		
	T		+			[^%]	100,0	4,1 ć	54,4 4	, 4 10,	8 1 0		0,9 14	.5	["] =	10127	101770	9'1	2,3	002101	00001	02.20	570075	15 4450	204020
		101 101	0 680 10	50		11/61	c 101	u 1	-	0 0	000				[6] ^L	101/01	101070	10,1766	10.00	000101	20001	7/00/0	C/70//C	10.4T0.7	0/7170
RD54	NbCI,	3 4		429 154	175		ν. Σ	₽ ₽	4 	₹ ?	~~ ~				dm [g]	7,1 /41	10,10/0	28,8	cuziu	10,1030 25,5	27	31,1	3,1352		
		tai X4	089 0	20		[%v]	100,0	4,4	4	7 88	8 2,0				[mut] s	2,7	1,8	4	4,3						
		999 €	820 10	35					$\vdash$						mv [g]	10,1679	10,1507	10,1568	10,17	10,467	10,0127	8,0712	38,4077	7±2.6	181±44
RD55	YCI <sub>a</sub>	s		119	175	[4/]	110,1	4,5 é	50,0	Ϋ́Β 2,1	0 7,8		12,0 16	3	m, [g]	10,1733	10,1532	10,1606	10,1759	10,0524	10,0174	8,079	33,5468		
		tai 660	0 820 10	35		[~%]	100.0	4.1	54.5 4	4.4	12		0.9 14	2	d <sub>m</sub> [mg] s [um]	5,4 2,3	2,5	3,8 2,2	5,9	-414,6	4,7	7,8	4,8609		
	Γ														m, ial	10,168	10,1276	101/01	10,1638	10,034	10,002	8,1017	36,3522	10±1.9	164±24
1910	UX	05 05	1 820	55 707	175	[I/h]	100,5	4,5	4	0 51	0 35,0				m, [g]	10,1849	10,1489	10,1354	10,1818	10,0541	10,0239	8,1238	31,5069		
0		t 250	820 10	25 00	2					_					dm [mg]	16,9	21,3	34,3	18	20,1	21,9	22,1	4,8453		
		9 <u></u>			1111	[%v]	100,0	4,5	4	,0 56,	7 34,8				s [µm]	2,1	2,8	3,1		3,6					
		029	820 10	35	1011			_							m <sub>v</sub> [g]	10,1773	10,1645	10,1637	10,192	10,1095	9,9763	8,0582	38,8196	11.8±4	382±84
RD:57	S(C)	s s		600	175	[1/4]	110,1	4,5 6	50,0 4	1,8 5,1	0 7,8		12,0 16	3	m, [g]	10,1798	10,1678	10,1679	10,1969	10,1148	9,9814	8,0636	33,5223		
6	500	t 650	820 10	35					+	-			+		d <sub>m</sub> [mg]	2,5	3,3	4,2	4,9	5,3	5,1	5,4	5,2973		
		!			1111	[%v]	100,0	4,1 5	54,5 4	1,4 4,1	1'2 5		0,9 14	5	s [hm]	9,0	-	۲. ۲.		2					
		029	0 820 10	35	1101										m <sub>v</sub> [g]	10,183	10,1658	10,0689	10,1563	10,1165	10,0063	8,0426	36,8359	15.8±4	382±84
RD58	SrCI,	s		608	175	[4/]	100,5	4,5	•	10 <u>2</u> 1'	0 35,0				m, [g]	10,1919	10,1733	10,083	10,1646	10,127	10,0229	8,0568	31,5886		
		ta 650	820 10	35						-					dm [mg]	8,9	7,5	14,1	8,3	10,5	16,6	14,2	5,2473		
		!				[%_]	100,0	4,5	4	1,0 56,	7 34,8				s [hm]	Ľ,	2,14	2,85		3,5					
		470	0 680 10	50						:					m^ [g]	10,1681	10,1634	10,1236	10,1305	10,123	10,0076	8,0621	56,4811	14.7±5.9	299±100
RD59	TaCl <sub>s</sub> -	s		431 154	1 175	[4]]	110,3	4,5 6	50,0	, E B	0 20		12,0 16	2	m, [9]	10/171	10,1666	10,1282	10,1359	10,1296	10,015	8,069	51,4941		
		ist 470	01 169 10	50		1				-					d <sub>m</sub> [mg]	~	3,2	4,6	5,4	6,6	7,4	6,9	4,9870		
		: !				[%^]	100,0	4,1 5	54,4 4	10,	0 1,8		0,9 14	5	s [µm]	1,14	1,42	1,99	2,6						
		300	00 7		11111					:					m_ [g]	10,1662	10,1406	10,1345	10,1139	10,1425	9,9875	8,01	59,8462		
RD60		s		- 276	175	[4]]	E'011	4 Ú	59,0	, ,	0 20	0(1	12,0 16	9.	m, [g]	10,1758	10,1598	10,1601	10,1305	10,1558	10,0013	8,0358 25	54,8639		
		tai Se	200 7	8	1010	[^%]	100,0	4,1 5	53.5 4,	4 10,	0 1,8	0,9 1	0,9 14,	5	s [um]	3,99	6,12	6,98	6,3	201	0,01	0/07	070//t		
		ř.	000	~						╞					mv [g]	10,1333	10,1428	10,1466	10,1326	10,1187	9,9547	8,1016	60,2738	12±4.3	239±138
DD41	TaiC.	≺ ₹ OS		124 154	1 75	[I/h]	101,3	4,5	4	(8 90)	0 2,0				m, [g]	10,1422	10,1584	10,1712	10,158	10,147	9,9877	8,1351	56,3606		
1002	i aci	± 470	1 200 1 0	50 400	2										d <sub>m</sub> [mg]	8,9	15,6	24,6	25,4	28,3	33	33,5	3,9132		
		F Nj		3		[%v]	100,0	4,4	4	(,7 88,	8 2,0				s [µm]	2,7	3,6	4,27	9						
		0 470	680 8	05	11111										mv [g]	10,1891	10,165	10,0789	10,1203	6,9997	9,9975	B,0029	59,5915		
RD62		s		425	45	[4/]	110,3	4,5 5	59,0 4	, 11, 8,	0 2,0	2	12,0 16	3	m, [g]	10,1926	10,1683	10,0811	10,1222	10,001	9,9987	8,0048	58,4804		
		t 470	0 680 8	20	1000				+	-			+		d <sub>m</sub> [mg]	3,5	3,3	2,2	1,9	۲. ۲.	1,2	1,9	1111/1		
		!			1111	[%v]	100,0	4,1 5	53,5 4	10,	0 1,8	0'6	0,9 14	5	8 [hm]	7,48	5,9	1,58	1,2						
		0 470	0 680 10	50	1010										mv [g]	10,1339	10,1278	10,1242	10,1421	9,9847	9,9894	B,1041	58,9794	13.2±6.8	261±87
RD63		s		425	175	[4]]	106/1	4,0 0	4	б Q	9′ <u>/</u> 0		\$2,0 25	3	m, [g]	10,1359	10,1307	10,1282	10,1469	9,9895	9,9938	8,114	54,3034		
		ist 470	0 692 10	50	11111	1 10	0001				F		00	0	dm [mg]	2 02 0	2'7	4 0	1 <sup>4</sup>	4,ŭ	4,4	6.6	4,6/60		
222						[^%]	I NNNI	4,1	4	74 47	11/ 9		20'Q 77		s [mu]	DC'N	471	0,06	//						

temperature (°C1 dep. 71 72 73 pc. pc. time total HC1 C	temperature [°C] dep. 71 72 73 pp. pp. time total HCI 0	mperature [°C] dep.	re [°C] dep. RE, RE, time total HC	dep. time total		total HCI	CH CH		SO <sub>2</sub> afte	r 5° on	rates [//	h]	4	Ē	eve	L04	EOJ	102		지 ~) [0]	os. 4]		Pre- cursor	Nanoinder H IGna1 + H	F IGnal + F
2000000 21 22 23 nul nu <sup>2</sup> [min] flow <sup>1101</sup> N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> <sup>112</sup> <sup>111</sup> <sup>111</sup> <sup>111</sup> <sup>111</sup>	21 22 20 ncl nc2 [min] flow 10 N2 CO2 H2 11 21 20	22 20 NLT NL2 [min] [flow 10 N2 CO2 H2 11 N1 20	<sup>nc1</sup> <sup>nc2</sup> [min] flow <sup>11C1</sup> N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> <sup>12</sup> <sup>1413</sup> <sup>CU1</sup>	[min] flow 1C N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> 11 2	flow IC N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> III CO	flow IC N2 CO2 H2 12 1413 CU	N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> H <sub>2</sub> M <sub>3</sub> M	N <sub>2</sub> CO <sub>2</sub> H <sub>2</sub> 12 14 12	5 H <sup>2</sup> - 12 M 2			_	Ĩ	į	sample	۲	∢	<	4	-0	υ	M٥	(in/out/loss)		r [oba] - r
110,1 4,5 60,0 4,8 5,0 7,8 7,12,0 12,0	,,,,,, [J/h] 110,1 4,5 60,0 4,8 5,0 7,8 /// 12,0	20, 1.2.0 7.8 [J/h] [110,1] 4.5 60,0 4.8 5.0 7.8 [12,0]	, [I/h] [110,1] 4,5 60,0] 4,8 5,0 7,8 7/12,0	12,0 1,1 110,1 4,5 60,0 4,8 5,0 7,8 12,0	[Uh] 110,1 4,5 60,0 4,8 5,0 7,8 // 12,0	110,1 4,5 60,0 4,8 5,0 7,8 7,20	4,5 60,0 4,8 5,0 7,8 12,0	0,0 4,8 5,0 7,8 12,0	1 5,0 7,8 1 12,0	7,8 12,0	12,0	0	16,0		10, 01										
4/0 000 1000 100 100 100 4,1 54,5 4,4 4,5 7,1 70,9 10,9 1	4/0 000 1000 1000 1/0 18/1 100,0 4,1 54,5 4,4 4,5 7,1 10,9 1	00 1000 171 100,0 4,1 54,5 4,4 4,5 7,1 100,9 1	[36v] 100,0 4,1 54,5 4,4 4,5 7,1 10,9 1	[36v] [00,0] 4,1 [54,5] 4,4 4,5 7,1 [30,9] 10,9 1	[38v] 100,0 4,1 54,5 4,4 4,5 7,1 10,9 1	100,0 4,1 54,5 4,4 4,5 7,1 10,9 1	4,1 54,5 4,4 4,5 7,1 10,9 1	4,5 4,4 4,5 7,1 10,9 1	1 4,5 7,1 10,9 1	1 6'01	10'6 1	6	4,5		s [um]										
	300 600											⊢			mv [g]	10,1693	10,1558	10,1662	10,2087	9,9987 1	10,0063	8,0454	38,2831		
YCl <sub>5</sub> × 273 175 [Vh] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 1	m     273     [1/h]     110,1     4,5     59,0     4,8     5,0     7,8     1,0     12,0     1	273 [175 [Uh] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 1	273 175 [Vh] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 1	175 [[/h] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 1	[J/h] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 1	110,1 4,5 59,0 4,8 5,0 7,8 <b>1,0</b> 12,0 1	4,5 59,0 4,8 5,0 7,8 <b>1,0</b> 12,0 1	9,0 4,8 5,0 7,8 1,0 12,0 1	3 5,0 7,8 <b>1,0</b> 12,0 1	7,8 1,0 12,0 1	1,0 12,0 1	-	6,0		m, [g] ما [mم]	10,1776 8.3	10,1702	10,1855	10,2349	20194	10,0281 21 8	8,0699 24 5	34,8022 3.4809		
· [型 300 500 700 [100 700 [154]] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 11,9 11	1     230     500     700     771     0.9     10.9     11	00 700 700 [56,1] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	[5%] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 1,	[% 1] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	[36v] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	3,6 4,4 4,5 7,1 0,9 10,9 14	1 4,5 7,1 0,9 10,9 1	21 0,9 10,9 12	0,9 10,9 14	6	5,		[mu] s	3,6	10,79	16,69	12,4	2017	2	2	20010		
												╞	í í		mv [g]	10,2067	10,1774	10,1738	10,1315	9,9714	6,9963	8,135	37,6982		
SrC12 0 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1	568     175     [[Vh]     110,1     4,5     59,0     4,8     5,0     7,8     1,0     12,0     16	568 175 [Vh] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 16	- 568 175 [Vh] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 16	175 [J/h] 110,1 4,5 59,0 4,8 5,0 7,8 1,0 12,0 16	[J/h] 110,1 4,5 59,0 4,8 5,0 7,8 <b>1,0</b> 12,0 16	110,1 4,5 59,0 4,8 5,0 7,8 <b>1,0</b> 12,0 16	4,5 59,0 4,8 5,0 7,8 <b>1,0</b> 12,0 16	9,0 4,8 5,0 7,8 <b>1,0</b> 12,0 16	3 5,0 7,8 1,0 12,0 16	7,8 1,0 12,0 16	1,0 12,0 16	20	3		m, [g] d [ma]	10,2171	10,1858 8.4	10,1787	10,1477	9,9932 21 B	10,0152	8,1581 23.1	32,5672 51310		
· 2 630 670 700 [54] [54] [100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 1.4	2     630     670     700     (%,1)     100,0     4,1     53,6     4,4     4,5     7,1     0,9     10,9     14	70 700 [35, 100, 4, 53, 4, 4, 5, 7, 0, 10, 10, 14	[%v] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	[%V] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14	[%,] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 1	100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 1	4,1 53,6 4,4 4,5 7,1 0,9 10,9 1	3,6 4,4 4,5 7,1 0,9 10,9 11	1 4,5 7,1 0,9 10,9 14	7,1 0,9 10,9 14	0,9 10,9 14	6 17	5		[mt] \$	3,17	2,73	2,45	1'1						
∑ 550 600 700 100 100 45 530 48 50 78 10 120 16	2 550 600 700 10 1101 45 530 48 50 78 10 120 15	00 700 700 10 10 10 10 12 52 53 18 50 78 10 120 15	1001 45 590 48 50 78 10 120 16	1101 4.5 59.0 4.8 5.0 2.8 1.0 12.0 15	[[kh] ]]10.1 4.5 59.0 4.8 5.0 7.8 1.0 12.0 15	110.1 4.5 59.0 4.8 5.0 7.8 1.0 12.0 15	4.5 59.0 4.8 5.0 7.8 10 12.0 16	30 48 50 78 10 120 16	1 50 ZB 10 120 16	7.8 10 12.0 16	1 0 12.0	0 16	9		mv [g] m [d]	10,0319	10,1246	10,1792	10,1298	9,9228 9.9404 1	9,992	8,0347 8.0561	37,1065 32.0564		
YCl <sub>3</sub> 756 600 200 495 175 77 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	550     600     795     175     •	00 700 495	- 495					· ·							d <sub>m</sub> [mg]	13,3	16	16,4	161	17,6	15,4	21,4	5,0501		
······································	2 000 000 100 100 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14,5	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	[%v] 100.0 4.1 53.6 4.4 4.5 7.1 0.9 10.9 14.5	[%v] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14,5	[%v] 100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14,5	100,0 4,1 53,6 4,4 4,5 7,1 0,9 10,9 14,5	4,1 53,6 4,4 4,5 7,1 0,9 10,9 14,5	3,6 4,4 4,5 7,1 0,9 10,9 14,5	L 4,5 7,1 0,9 10,9 14,5	7,1 0,9 10,9 14,5	0,9 10,9 14,5	9 14,5			s [hm]	3,17	6,04	77,77	9,9						
2 470 680 1050 11100 11003 45 1100 48 000 20	0 470 680 1050 1141 1033 45 45 45 20 20	B0 1050 80 1050 45 48 000 20 20 20 20 20 20 20 20 20 20 20 20	1000 45 1000 1000 1000 1000 1000 1000 10	1001 1002 45 000 20	14H1	1833 45 18 800 30	45						ann	2	mv [g]	10,1141	10,1151	10,1728	10,1702	10,0052	9,9747	8,0595 e 0004	58,6506	12.1±6.1	230±83
CH, + + + 435 175 171 172 720 720 720 270 270 270 270 270 270 2	435	435 175 175 172 172 172 172 172 172 172 172 172 172	+ 435 1 75 1 75 1 1 25 1 1 25 1 1 25 1 25 1										an	3	10 10 10 10 10 10 10 10 10 10 10 10 10 1	272	101	01.0	0407/01		1000/01	101			
· 프 470 701 1050 [18.4] 100,0 4,4 / 20 2.0	호 470 701 1050 150 158 1000 4,4 17 85,0 2,0 167 17	01 1050	[56.0] 100.0] 4.4 // 4.7 88.0 2.0 //	[%] 100.0 4,4 /// 4,7 88.0 2.0 ///	[%] 100,0 4,4 /// 4,7 88,0 2,0 ///	100.0 4.4 /// 4.7 88.0 2.0 ////	4,4 /// 4,7 88,0 2,0 ////	4,7 88,0 2,0	1 88,0 2,0 /////////////////////////////////	2.0			(nur	0,1	s [http://ww	3,6	2,88	4,46	5		5		1,000		
															mv [g]	10,1972	10,0634	10,1182	10,1401	9,9834	1/2 19'6	8,0448	61,8288	13.9±9.3	322±160
Cu 8 4/0 600 1030 1031 175 106,3 4,5 4,5 90,0 2,0 4,6 70,0 5	8 4/0 500 1000 100 100 100 100 100 100 20 100 20 10 20 10 20 10 20 10 20 10 20 10 10 10 10 10 10 10 10 10 10 10 10 10	20 1000 100 100 100 100 100 100 100 100	4,8 90,0 2,0 175 106,3 4,5 4,5 4,8 90,0 2,0 2,0 5	1 TE [U/h] 106,3 4,5 4,8 90,0 2,0 2,0 5	IVh1 106,3 4,5 4,8 90,0 2,0 2,0 5	106,3 4,5 4,8 90,0 2,0 2,0 5	4,5 4,8 90,0 2,0 2,0 5	4,8 90,0 2,0 5	8 90.0 2.0 5 5	2,0 5	5	5		Q	m, [g]	10,2097	10,08	10,1436	10,1798	10,0188	9,6488	8,0798	57,1090		
													m		d <sub>m</sub> [mg]	12,5	16,6	25,4	39,7	35,4	31,7	35	4,7198		
1 <sup>-22</sup> 1 <sup>-1</sup> 1 <sup>-1</sup> 1 <sup>-1</sup> [35,1] [100,0] 4,2 [11,2] 4,5 [84,7] 1,9 [11,1] 4,4	2 7. 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 4 4 4 7 4 7 4 7 4 7 7 7 7 7 7 7 7 4 7 7 4 7 7 4 7	1 20 1 20 1 20 1 20 1 20 1 2 2 2 2 2 2 2	[18v] [18v] [100,0] 4,2 [11,5] 84,7 1,9 [11,1] 4,4 4,5	[18v] [100,0] 4,2 []] 4,5 [84,7] 1,9 [] 4,9 4	[154] [100,0] 4,2 [7] 4,5 [84,7] 1,9 [7] 1,9 [7] 4	100.0 4.2 1/ 4.5 84.7 1.9 1/ 4.	4,2 11 4,5 84,7 1,9 11 4	4,5 84,7 1,9 1,9 4	5 84.7 1.9 1.9 4	1,9 11,9 4	4	4	4	7	s [µm]	1,7	2,3	2,2	8,5						
															mv [g]	10,1163	10,063	10,1135	10,1566	9,992	9,9541	7,9798	63,5033	13±3.7	337±136
ccr × 4.8 90.0 2.0 17c [1/h] 101.3 4.5 // 4.8 90.0 2.0 //	2 7 00 100 100 100 100 100 100 100 100 10	20 100 100 100 100 100 100 20 100 100 10	1 423 22 1 75 [Uh] 101,3 4,5 4,8 90,0 2.0	1 75 [I/h] 101,3 4,5 24,8 4,8 90,0 2.0	[I/h] 101.3 4.5 4.8 90.0 2.0 2.0	101.3 4.5 4.8 90.0 2.0	4.5 4.8 90.0 2.0	4,8 90,0 2,0	3 90.0 2.0 Z	2.0					m, [g]	10,1281	10,08	10,1387	10,1979	10,0405	6,9983	8,0265	59,1830		
													<u>))))</u>		d <sub>m</sub> [mg]	11,8	17	25,2	41,3	48,5	44,2	46,7	4,3203		
······································	20 4/0 /02 1030 [36,] 100,0 4,4 /// 4,7 88,8 2,0 /// // // //	02 1030 [36.] 100.0 4,4 /// 86.8 2.0 /// //	[%,] 100,0 4,4 /// 4,7 88,8 2,0 /// //	[% <sub>1</sub> ] 100.0 4,4 //// 4,7 88,8 2,0 ////	[%v] 100.0 4,4 //// 4,7 88,8 2,0 ////////	100,0 4,4 /// 4,7 88,8 2,0 /// //	4,4 //// 4,7 88,8 2,0 ///////////////////////////////////	4,7 88,8 2,0	7 88,8 2,0 M	2,0					8 [hm]	9'1	2	3,5	4,5						
													))III		mv [g]	10,1581	10,1714	101	10,1619	9,9736	9,9251	7,9371	60,5062	8.5±1.6	102±22
cici. <sup>20</sup> <sup>4</sup> / <sup>10</sup> <sup>100</sup> <sup>101</sup> <sup>101</sup> <sup>101</sup> <sup>102</sup> <sup>1175</sup> <sup>1175</sup> <sup>1175</sup> <sup>1175</sup> <sup>1175</sup> <sup>1175</sup> <sup>1170</sup> <sup>1170</sup> <sup>1170</sup> <sup>1170</sup> <sup>1170</sup>	2 4.0 57.0 35.0 175 1/hl 100.5 4.5 4.6 4.0 57.0 35.0 175 176	4,0 57,0 35,0 75,0 77,0 75,0 75,0 75,0 75,0 75,0 7	431 38 175 [Vh] 100.5 4.5 <b>[ 4.0 57.0 35.0 </b>	1 75 [Uh] 100,5 4,5 <b>4</b> ,0 57,0 35,0 <b>3</b> 5,0	[I/h] 100,5 4,5 <b>4,0 57,0 35,0</b>	100,5 4,5 4,0 57,0 35,0 75,0	4.5 4.0 57.0 35.0	4,0 57,0 35,0	57.0 35.0 S	35.0			ditte		m, [g]	10,1651	10,181	10,117	10,1885	10,0102	9,9878	7,9686	55,7265		
													diffe		d <sub>m</sub> [mg]	7	9'6	17	26,6	36,6	62,7	31,5	4,7797		
· 2 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	[36v] [100,0] 4,5 [///] 4,0 [56,7] 34,8 [////]	[% <sub>1</sub> ] 100.0 4,5 //// 4,0 56,7 34,8 ////////////////////////////////////	[154.] 100.0 4.5 [7] 4.0 56.7 34.8 [7]	100.0 4.5 1/1 4.0 56.7 34.8 1/1 4.	4,5 ///// 4,0   56,7   34,8 ////////////////////////////////////	4,0 56,7 34,8 7 34,8	1 56.7 34.8	34,8			<i>illi</i>		s [µm]	2,5	3,6	6,2	7,6						
													ditte		mv [g]	10,1544	10,1674	10,129	10,0141	10,0185	9,954	8,0207	61,3684	2.4±1.2	26±11
SiCL, X 7/0 000 100 120 175 10hl 100,5 4,5 4,9 80,0 12,0 12,0	x 7.0 00 12.0 17.5 [Vh] 100.5 4.5 <b>4.0 80.0 12.0</b>	4,0 80,0 12,0 17,5 1/h1 100,5 4,5 4,0 80,0 12,0 12,0	427 28 175 [Uh] 100,5 4,5 <b>4,9 80,0 12,0</b>	175 [Uh] 100,5 4,5 <b>4,0 80,0 12,0</b>	[Vh] 100.5 4.5 4.0 80.0 12.0	100,5 4,5 4,0 80,0 12,0	4,5 4,0 80,0 12,0	4.0 80.0 12.0	1 80.0 12.0	12.0			<del>,////</del>		m, [g]	10,1633	10,1768	10,1507	10,0591	10,0784	10,0258	8,0639	57,3671		
표 4.70 704 1050	1 470 704 1050	04 1050													d <sub>m</sub> [mg]	8,9	9,4	21,7	45	59,9	д,8	43,2	4,0013		
[%v] 100:0 4.5 /// 4.0 79.6 111.9 ///	- [% <sub>v</sub> ] 100.0 4.5 /// 4.0 79.6 11.9 //	[% <sub>1</sub> ] 100.0 4.5 //// 4.0 79.6 11.9 ////	[35,v] [100,0] 4,5 4,0 79,6 11,9	[35v] 100,0 4,5 4,0 79,6 11,9	[3kv] 100,0 4,5 /// 4,0 79,6 11,9 ///	100,0 4,5 /// 4,0 79,6 11,9 ///	4,5 4,0 79,6 11,9	4,0 79,6 11,9	0 79.6 11.9	11.9 1 1.9	~~				s [hm]	3,6	3,9	6	17,5						
sicl, 👼 470 680 1050		80 1050											,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		mv [g]	10,1988	10,1999	10,184	10,1392	9,8822	9,9764	B,0414	60,1612	1.3±0.5	23±10
4.0 83.0 5.0 175 [01] 101.5 4.5 4.0 83.0 5.0 [17]	4.0 83.0 5.0 175 [Uni] 101.5 4.5 [4.0 83.0 5.0 [4.0 [4.0 [4.0 [4.0 [4.0 [4.0 [4.0 [4	433 26 175 [Uh] [UL2] 4.5 4.0 83,0 5.0 [	433 26 175 [WN] 101.5 4.5 4.9 83.0 5.0		1/h] 1/0.1 2 4.0 83.0 5.0 [1/h]	101.5 4.5 4.0 83.0 5.0 F	4,0 83,0 5,0 (c) 4,0 (	4.0 83.0 5.0		n's	-,	-,		2	m, [g] A [ma]	10,2116	14.3	20 0	10,2219 82.7	9,994	104.4	0,132 00.4	5 6650		
CH4 12 470 702 1050 181 1000 44 11 39 81.8 4.9	± 470 702 1050 1851 100.0 4.4 /// 3.9 81.8 4.9 ///	02 1050 18.1 100.0 4.4 /// 3.9 61.8 4.9 /// 3	[₩1] 100.0 4.4 /// 3.9 B1.8 4.9 ///	[%] 100.0 4.4 /// 3.9 81.8 4.9 ///	[%.] 100.0 4.4 (3.9 81.8 4.9 (100.0 1.4 (100	100.0 4.4 3.9 81.8 4.9	44 3.9 81.8 4.9	39 61.6 4.9	· 81.8 4.9	4.9			(Van	4.9	s [um]	5,4	7	12	35	2		n'^/	7000/0		
															m. ial	10,1153	10,1483	10,1704	10.1713	10.0259	9.9716	7,9369	42,9833	16.9±7	372±157
0     650     820     1035     1101     4.5     4.0     7.6     1.70 <th>0 650 820 1035 11111 1101 45 200 48 50 78 1101 1101</th> <th>20 1035 1001 1001 10 100 10 10 10 10 10 100 10</th> <td></td> <td></td> <td></td> <td></td> <td>15 200 40 50 70 100 120</td> <td>00 1 1 0 1 1 0 1 0 0 1 0 0 1 0 0 1 0</td> <td>2 2 3 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2</td> <td>70 120</td> <td>1001</td> <td>1</td> <td></td> <td></td> <td></td> <td>101101</td> <td>101501</td> <td>1017/01</td> <td>01/101</td> <td>00000</td> <td>0.0200</td> <td>20712</td> <td>000.04</td> <td></td> <td></td>	0 650 820 1035 11111 1101 45 200 48 50 78 1101 1101	20 1035 1001 1001 10 100 10 10 10 10 10 100 10					15 200 40 50 70 100 120	00 1 1 0 1 1 0 1 0 0 1 0 0 1 0 0 1 0	2 2 3 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	70 120	1001	1				101101	101501	1017/01	01/101	00000	0.0200	20712	000.04		
MnCl <sub>2</sub>	000 175 175 000 4,4 000 4,4 000 175 175 000 4,4 000 000 000 000 000 000 000 000	602 175 110/1 4/3 60/1 4/9 3/9 //3 12/9 10/9	1 602 1 75 1 M 110,1 4,3 60,0 4,6 3,0 1,7 1 1 20 1 20	175 a./ u.c a.4 u.o c.4 i.u.i mil 217						12/1 10/1	0'01 0'71	2 2 2	11111		m, [g]	10,118/	10,1521	10,1 /68	10,1758	6750/01	46/4/4	7,9415			
#1 650 B20 1035	t 650 820 1035												114		d <sub>m</sub> [mg]	4,0	Ω''n	0,4	D,4		5,4	0,4			
··· ··· ··· ··· ··· ··· ··· · · ··· · ·		[%v] 100.0 4.1 54.5 4.4 4.5 7.1 [10.9 14.5	[%y] [100,0] 4,1 [54,5] 4,4 [4,5] 7,1 [[] 10,9 [14,5]	[%v] 100.0 4.1 54.5 4.4 4.5 7.1 [[10.9] 14.5	[%v] 100,0 4,1 54,5 4,4 4,5 7,1 7,1 10,9 14,5	100,0 4,1 54,5 4,4 4,5 7,1 10,9 14,5	4,1 54,5 4,4 4,5 7,1 10,9 14,5	4,5 4,4 4,5 7,1 10,9 14,5	1 4,5 7,1 10,9 14,5	7,1 10,9 14,5	10,9 14,5	9 14,5			s [µm]	0,9	1,4	1,5	2,6						
													1111.		m, [g]	10,1759	10,1048	10,1814	10,1558	10,0364	10	8,066	41,2754	13.7±5.7	284±77
Macci 2 20 27.0 35.0 175 100.5 4.5 4.0 35.0 35.0 25.0	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	200 200 172 1/hl 100,5 4,5 4,0 57,0 35,0	2000 1 775 1 100,5 4,5 4,5 4,0 57,0 35,0	1 TE [1/h] 100,5 4,5 4,0 57,0 35,0	I/hl 100,5 4,5 4,0 57,0 35,0	100.5 4.5 4.0 57.0 35.0	4,5 4,0 57,0 35,0	4.0 57.0 35.0	0 57.0 35.0	35.0					m, [g]	10,1978	10,1267	10,2073	10,17	10,0487	10,0141	8,0873			
															d <sub>m</sub> [mg]	21,9	21,9	25,9	14,2	12,3	14,1	21,3			
24,0 1000 1000 1000 1000 1000 1000 1000 1	2, 200 020 020 020 020 020 020 020 020 0	20 1035 [%,] 100,0 4,5 [/// 4,0 5,7 34,8 [///	[%] 100,0 4,5 /// 4,0 56,7 34,8	[%v] 100/0 4,5 /// 4/0 56,7 34,8	[%] 100,0 4,5 /// 4,0 56,7 34,8 ///	100,0 4,5 4,0 56,7 34,8	4.5 4.0 56.7 34,8	4,0 56,7 34,8	1 56,7 34,8	34,8					s [hm]	1,8	2,9	3,7	3.8						
						AND		A CONTRACTOR OF	A CONTRACTOR OF			٩.													

$ \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1$	tem	ε	peratr	Jre [°C]	dep.			¢	gas fl	low rates	[I/h]		-	-	-	-				Pre	Nanoind	entation
	71 70	- 2	5	PC, PC,	time		total T	2	2 atter 5	н с	NH. Ar. Ar.	CH.	-	04	2 7		9   	l (~ Pos. 4)		CURA	OF HIGARIHH	E [Cna] + E
(N)     (N) <th>1</th> <th>1</th> <th>2</th> <th></th> <th>[uiu]</th> <th></th> <th>flow .</th> <th>ź</th> <th>°0</th> <th>H, H</th> <th>7m / 1m / 2mm</th> <th>samp</th> <th><u>e</u></th> <th>۲ ۲</th> <th>&lt;</th> <th>4</th> <th></th> <th>0</th> <th>Ň</th> <th>o (in/out/l</th> <th>[020]</th> <th>1 [ [ 2 2] ]</th>	1	1	2		[uiu]		flow .	ź	°0	H, H	7m / 1m / 2mm	samp	<u>e</u>	۲ ۲	<	4		0	Ň	o (in/out/l	[020]	1 [ [ 2 2] ]
		j 0	100		175	[I/H]	110,1	1,5 60,0	4,8	5,0 7,8	12,0 16,0	S. M.	25									
000     010 <th>4/7</th> <th>3</th> <th>3</th> <th></th> <th>3</th> <th>[<sup>2</sup>%]</th> <th>100,0</th> <th>LJ 54,5</th> <th>4,4</th> <th>4,5 7,1</th> <th>10,9 14,5</th> <th>2440 2440</th> <th>N.</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	4/7	3	3		3	[ <sup>2</sup> %]	100,0	LJ 54,5	4,4	4,5 7,1	10,9 14,5	2440 2440	N.									
000000000000000000000000000000000000	087 UL 7	â	1050									mv li	g] 10,	101 5081	91/01 199	21/01 22	25 9,975	96 9,950	36 8,09	37 61,01	72 6.6±1.4	51±8
10     10<	000	8	5	104 20	145	[1/h]	101,3	5	6 9 9 0	(7,0 5,0		m, l	g] 10,	1827 10,1	7 10,16	27 10,178	84 9,981	1 9,961	5 8,10	02 56,71	44	
Min.     Min. <th< td=""><th>470 701</th><td>Ę</td><td>1050</td><td></td><td>ł</td><td></td><td></td><td></td><td></td><td></td><td></td><td>d<sub>m</sub> [r</td><td>1g] 2</td><td>2,2 3,5</td><td>5,7</td><td>5,9</td><td>7,5</td><td>7,9</td><td>6,5</td><td>5 4,302</td><td>28</td><td></td></th<>	470 701	Ę	1050		ł							d <sub>m</sub> [r	1g] 2	2,2 3,5	5,7	5,9	7,5	7,9	6,5	5 4,302	28	
1000000000000000000000000000000000000		5	ŝ			[%v]	1 00,0	4	4,7	5,9 4,9		s [hr	[u	5, L	°-		2,7	_				
Model     Model <th< th=""><th>695 820</th><th>8</th><th>102</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th>m<sub>v</sub> i</th><th>0] [0]</th><th>1701 10/1</th><th>27 10,15</th><th>43 10,191</th><th>17 9,941</th><th>6 9,965</th><th>98 8,03</th><th>27 35,47</th><th>741 9.3±8.1</th><th>234±145</th></th<>	695 820	8	102									m <sub>v</sub> i	0] [0]	1701 10/1	27 10,15	43 10,191	17 9,941	6 9,965	98 8,03	27 35,47	741 9.3±8.1	234±145
100     100 <th></th> <td></td> <td></td> <td>650</td> <td>175</td> <td>9</td> <td>100,5</td> <td>5.                                     </td> <td>4,0</td> <td>7,0 35,0</td> <td></td> <td>- un</td> <td>a] 10,</td> <td>1787 10,13</td> <td>10,11</td> <td>74 10,201</td> <td>14 9,950</td> <td>9,978</td> <td>35 8,04</td> <td>8</td> <td></td> <td></td>				650	175	9	100,5	5. 	4,0	7,0 35,0		- un	a] 10,	1787 10,13	10,11	74 10,201	14 9,950	9,978	35 8,04	8		
100     100 <th>695 820</th> <td>320</td> <td>1036</td> <td><u>19</u></td> <td></td> <td>[^%]</td> <td>100.0</td> <td>5</td> <td>4,0 5</td> <td>6.7 34.6</td> <td></td> <td>am Lin s Lun</td> <td></td> <td>0'0 9'</td> <td>2 m</td> <td>4,1</td> <td>217</td> <td>//0</td> <td><u>.</u></td> <td>2</td> <td></td> <td></td>	695 820	320	1036	<u>19</u>		[^%]	100.0	5	4,0 5	6.7 34.6		am Lin s Lun		0'0 9'	2 m	4,1	217	//0	<u>.</u>	2		
	007 011	ð										mv li	a] 10,	0373 10,0E	327 10,12	51 10,18	32 9,986	6,987	76 8,09	03 58,92	21 18.5±9.5	209±300
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	470 713	- 6	1050			ļ				1		ш_тр	[0]	3,4 22,	6 24,9	66'3	202	9 1/1	72,	2 5,307	20	
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10     10     103     145     10     103						[Anr]	~~~~	4	D F	2				2101	> 101	10101	000	0001	202	ro 02	110477	2004147
1     1     1     0     1     0     1     0     1     0     6     5	470 68	<u>0</u>	0 1050		1000	[I/h]	108,3 4	5. 1	48	0.0 2.0		7.0 m. l	al 10	1555 10,22	221 10.22	71 10.24	20101 20101	00 10/14 00/14	07 8.05	03 54,58	14:0±0.7	1417000
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Molecane	4/0 /03	ő.	, 102		11111	[%]	100,0	12	4,4	3,1 1,8		ur] s [hu	[]	2,5 4,5	4	9						
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	1/1- 0.07	1	8	070	175	[1/h]	110,3 4	1,5 59,0	4,8 1	1,0 2,0	1,0 12,0 16,0	m, la	g] 10,	1305 10,14	13 10,18	84 10,14;	28 10,03	25 10,04;	31 8,08	145 55,27	39	
$ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	288 470	K	1 600	3	2							dm [rr	1g] 4	1,2 9,3	11,5	9 14,7	7 13,1	9, LL	3 14,	,1 4,529	06	
1000000000000000000000000000000000000	74 47	Ş I	8		1111	[‰]	1 00,0	1,1 53,5	4,4 1	0,0 1,8	0,9 10,9 14,5	uri] s	u]	2 7,4	1 8,9	13						
$ \  \  \  \  \  \  \ \ \ \ \ \ \ \ \ \$	470 AB	0	0 1050									-mv [	g] 10,	1814 10,1:	32 10,05	84 10,180	37 10,04:	22 9,955	59 8,02	13 59,31	28 6.5±1	55±6
$ \left  10^{\circ} \right  10^{\circ} \right  \left  10^{\circ} \right  10^{\circ} \right  \left  10^{\circ} \right  10^{\circ} \right  10^{\circ} \left		ξI		430 30	1.75	[1/h]	100,5 4	5	4,0 8	4,0 8,0		m, la	g] 10,	1929 10,14	10,09	51 10,250	37 10,13	62 10,00	99 8,11	22 53,80	067	
$ \left  100 \\ $	470 711		1050	Ì	2							d <sub>m</sub> [n	1g] ]	1,5 17,	4 36,	7 70	94	53,1	- 20	9 5,506	61	
$ \frac{100}{100} + \frac{1}{10} + \frac{1}{$	>		5			[%^]	100,0	.5	4,0	3,6 8,0		uri] s	[]	5,3	7,8	_	51,2		_			
$ \frac{1}{1000} \frac{1}{100} \frac{1}{100} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac{1}{100} \frac{1}{10} \frac$	470 680	ğ	01050	_								m <sub>v</sub> l	[] [0,	1303 10,10	078 10,13	07 10,130	02 9,987	20'00'	53 7,98	24 59,28	318 8.6±1.4	150±20
$ \left[ 100 \\ $				438 30	175	[4]	100,5	2;	4.0	6,0 3,0		ď	[] []	1451 10,13	349 10,18	17 10,21	26 10,04	93 10,06	83 8,06	42 54,39	214	
10-0     10-0 <th< th=""><th>470 711</th><th>E</th><th>1050</th><th></th><th></th><th>[~%]</th><th>100.0</th><th>5</th><th>40</th><th>8.6 3.0</th><th></th><th>dm In s Lur</th><th></th><th>4,8 27, 3,1 13</th><th>22.5</th><th>02,4</th><th>4 61/2 11/2</th><th>63</th><th>ă</th><th>8 4,89(</th><th>04</th><th></th></th<>	470 711	E	1050			[~%]	100.0	5	40	8.6 3.0		dm In s Lur		4,8 27, 3,1 13	22.5	02,4	4 61/2 11/2	63	ă	8 4,89(	04	
1000     175     100.5     4.5     0.0     5.0     5.0     5.0     5.1     5.1     5.0     5.1<	0, 91,											m	0]	1439 10,13	305 10,18	59 10,17	72 10,00	82 9,975	96 7,93	157 59,48	343 15.1±5.5	323±102
$ \left  10^{5} \right  10^{5} \right  \left  10$	4/0 60	<u> </u>	1 1 1	2	175	[1/14]	100,5 4	<u>s</u>	4,0 5	7,0 35,0		m, İn	ol 10,	1498 10,1.	41 10,20	23 10,18	63 10,02	19 9,984	43 7,95	01 54,92	185	
$ \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{1000} + \frac{1}{10000} + \frac{1}{10000} + \frac{1}{10000} + \frac{1}{100000} + \frac{1}{1$	170 71	1.5	1050		2							dm In	1g] 6	59 10,	5 16,	14,3	3 13,7	10/2	7 14,	4 4,556	58	
1000     1010     1015     4.5     10.5     4.5     10.0     10.5     4.5     10.0     10.0     4.0     9.00     1.0     4.0     9.00     1.0     4.0     9.00     1.0     4.0     9.00     6.3±2     6.3±2     6.4±2     6.4±2     6.4±2     6.4±2     6.4±2     6.4±2     10.0     10.0     10.05     10.0     10.05     10.012     10.012     10.125     10.12			- -			[%v]	1 00,0	l,5	4,0 5	i6,7 34,6	3 V X X	s [hr	n] (i	3,4 3,6	3 5,1	9						
1/10     1/2     1/10     1/2 </td <th>470 68</th> <td><u> </u></td> <td>0 1050</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>mv li</td> <td>g] 10,2</td> <td>2004 10,12</td> <td>202 10,1</td> <td>7 10,113</td> <td>29 9,960</td> <td>10'01 9</td> <td>04 8,08</td> <td>94 59,89</td> <td>05 6.3±2</td> <td>66±12</td>	470 68	<u> </u>	0 1050									mv li	g] 10,2	2004 10,12	202 10,1	7 10,113	29 9,960	10'01 9	04 8,08	94 59,89	05 6.3±2	66±12
2 1050 1 15 15 15 15 15 15 15 15 15 15 15 15 1				440 30	175	[l/h]	101,5	.5	4.0 9	0,0 2,0	10	m, li	g] 10,	2132 10,13	85 10,19	56 10,13,	55 9,985	52 10,03	32 8,11	01 54,90	067	
1000     1100     14     39     88.7     20     10     11.6     11.7     11.7     11.6     11.6     11.7     11.7 <th>470 71</th> <td>Ē</td> <td>1050</td> <td>· · · · · · · · · · · · · · · · · · ·</td> <td>2</td> <td></td> <td></td> <td></td> <td></td> <td>_</td> <td></td> <td>dm [r</td> <td>1g] [j</td> <td>2,8 18,</td> <td>3 25,4</td> <td>5 22,6</td> <td>6 24,7</td> <td>7 22,6</td> <td>30,</td> <td>.7 4,980</td> <td>R</td> <td></td>	470 71	Ē	1050	· · · · · · · · · · · · · · · · · · ·	2					_		dm [r	1g] [j	2,8 18,	3 25,4	5 22,6	6 24,7	7 22,6	30,	.7 4,980	R	
1050     105     105     105     105     105     101     100.5     10.005     10.14.7     10.1631     10.0005     8.037     59.3857     6±2.2     209±70       1050     175     10172     10.1725     10.1772     10.0326     54.5372     203±70     54.5372     209±70     209±70       1050     1772     10.1772     10.0322     10.1772     10.0322     54.5372     54.5372     209±70       1050     1772     10.1772     10.0262     10.1772     10.0272     54.5372     54.5372     209±70	7		-			[%v]	100,0	.4	3,9 8	8,7 2,0	1.0	s [hr	<u>ا</u>	12,	5 18,		9'11		_			
1     17     17     17     17     17     10026     10,1702     10,1702     10,1702     10,0202     4,6322     4,6322       1     10060     417     187     10,1702     10,1702     10,0202     10,0202     5,5676     54,5372       1     10600     4,7     14     23     14,1     28     27,8     30,6     4,8465	470 45	<u> </u>	0 1050									m. li	g] 10,	0275 10,13	867 10,14	79 10,16	31 10,00	02 10,00	05 8,00	37 59,38	6±2.2	209±70
1050 <sup>11</sup> 23 14.1 28 29.6 30.6 4.8485	200 2	ξI		417 187	175	[l/h]	100,5	5. 	4,0 8	9,0 3,0	_	m, li	a] 10,	0344 10,15	07 10,17	09 10,17,	72 10,02	82 10,03	03 8,06	76 54,53	372	
	470 71	F	1 1050		2							dm [17	1g] 6	.9 14	8	14,1	28	29,6	Ř	6 4,846	85	