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Thin film deposition on powder surfaces using atmospheric pressure discharge

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Abstract. The deposition of SiOx containing films on NaCl and KBr particles in dielectric barrier discharge under atmospheric pressure was investigated. As precursor hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS) in argon-oxygen gas mixtures were used. The deposited layers were studied by means of light microscopy, SEM and XPS investigations. The particles could be completely covered by SiOx. With increasing oxygen content in the coating the carbon content decreases.

1. Introduction

The dielectric barrier discharge (DBD) at atmospheric pressure has been used for many technical applications, for example ozone generation, gas cleaning, surface treatment of foils and fabrics [1]. Atmospheric pressure plasmas for surface treatment of materials become more and more important because in contrast to low pressure plasmas no vacuum devices are necessary. Therefore, batch processing can be avoided and treatment processes can be easily integrated into production lines.

For more than ten years the deposition of organosilicon layers on flat substrates has been studied by the use of various monomers [2, 3]. In this paper, the deposition of silicon containing thin films on powder particles is described. These coatings can be used as protection layers for luminescent particles or pigments against corrosion and humidity. Some pharmaceuticals need barriers for a slow release of the agent, too. The present contribution focuses on the deposition of SiO_x containing layers on salt particles which served as model substances for powders. Hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS), respectively, were used as precursor.

For the modification of powder surfaces special techniques have to be applied in order to realize a homogeneous treatment. Therefore, the planar dielectric barrier discharge arrangement was combined with a vibrating conveyor device. The composition of coatings and the influence of the thickness of the dielectric barrier were investigated.

2. Experimental

In Fig. 1 the schematic diagram of the experimental apparatus is shown. The powder treatment system consists of three major parts: a mechanically agitating chamber for plasma treatment, a gas feeding system and a power supply. On the bottom of the treatment chamber a planar surface dielectric barrier discharge arrangement is fixed. The discharge arrangement is made from a printed circuit board. One side of this circuit board is completely covered by a copper layer and represents the ground electrode. On the opposite side is the high voltage electrode consisting of an etched copper layer. Between the stripes of the high voltage electrode a filamentary surface discharge is generated. The bulk material of the circuit board consists of non-conducting material and represents the dielectric barrier. On the top of the

treatment chamber a gas distributor for homogenous gas injection is mounted. The chamber can be mechanically agitated by an electromagnet to move the powder through the plasma zone of the surface discharge (Fig. 1).
The atmospheric surface discharge is driven by a medium frequency pulse generator (Fourier Synthesis Pulse Generator, Ingenieurbüro Dr. Jürgen Klein) which has a frequency range between 1 Hz and 20 kHz and a maximum voltage of 20 KV. The pulse generator is controlled by a frequency generator (AFG 310 Sony/Tektronics).

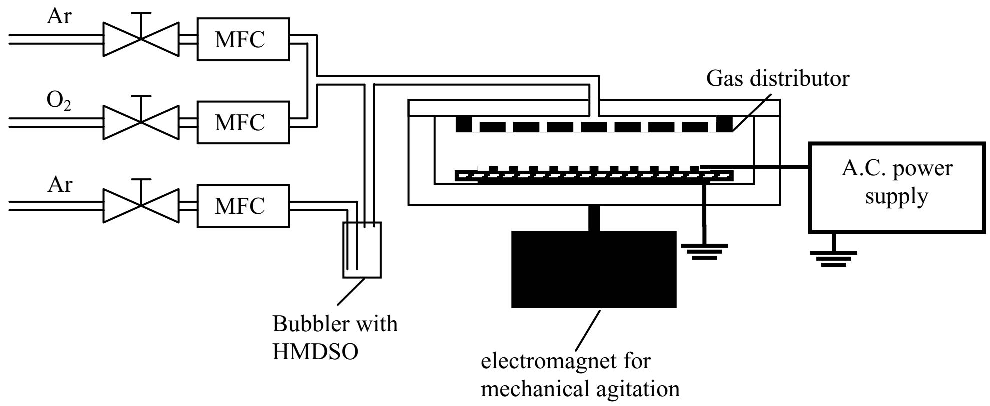

Fig. 1 Scheme of the experimental set-up

Oxygen and argon are used as plasma gas. The liquid precursors hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS) respectively are introduced by feeding argon through a bubbler. Plasma treatments were carried out under following conditions:

Table 1 Treatment conditions

TEOS concentration [vol-ppm]	HMDSO concentration [vol-ppm]	Carrier gas concentration [vol-%]	O_2 concentration [vol-%]	Gas flow [sccm]	Treatment time [min]
2000	/	Ar 95	4.8	210	30
/	1600	Ar 0..100	0..100	300	10

Silicon oxide containing layers have been deposited onto NaCL and KBr powder used as model substances. Dielectric barriers with two different thicknesses (0.5 and 1 mm) were used. The treated particles were characterized by light microscopy and photo electron spectroscopy (XPS).

3. Results and Discussion

Deposition in TEOS-Ar-O_2 on NaCl

NaCl powder was coated by SiO_x using TEOS precursor. The coated salt particles were examined with optical light microscopy and scanning electron microscope. In Fig. 2 SiO_x coated crystals are shown. The NaCl crystals are completely covered by the layer. Later, the NaCl was removed by solving in water. Only a box consisting of the SiO_x containing material remains (Fig 3). Apparently, there are some holes in the layer which make a penetration of water into the box possible. Hence, tiny (micro) glass boxes have been prepared.

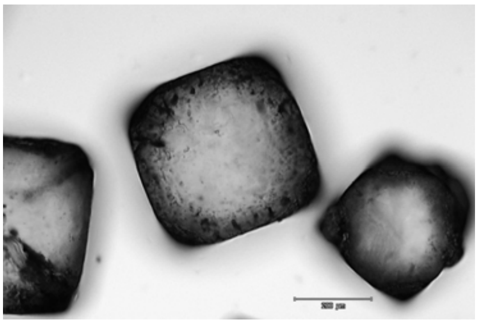

Fig. 2 NaCl particles coated in TEOS-Ar-O_2

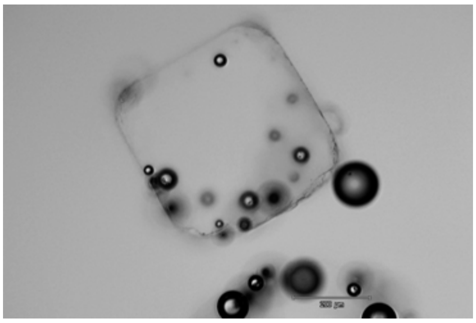

Fig. 3 Remaining coating after dissolution of NaCl crystal in water. The coating was deposited in TEOS-Ar-O_2.

Deposition in HMDSO-Ar-O_2 on KBr

The composition of the deposited layer was investigated by XPS measurements (Fig. 4 and 5). The plasma treatments were performed at four different oxygen concentrations in the range of 10-100 vol.-%.

The Si content hardly depends on the oxygen gas concentration. The content of carbon and oxygen changes with oxygen gas concentration, too. Mainly, with decreasing oxygen supply the carbon content increases. With changing gas concentration in the discharge various effects influence the deposition process. On one hand, with increasing oxygen concentration the oxidation strength increases. On the other hand, internal properties of the discharge change and can have an effect on the oxidation process.

Additionally, the carbon content of coatings deposited using the thinner dielectric barrier is more than in coatings deposited using the thicker dielectric barrier.

To clarify this effect, the deposition process was carried out at two different discharge voltages (6.15 kV, 8.23 kV) using dielectric barriers with two different thicknesses (Fig. 6).

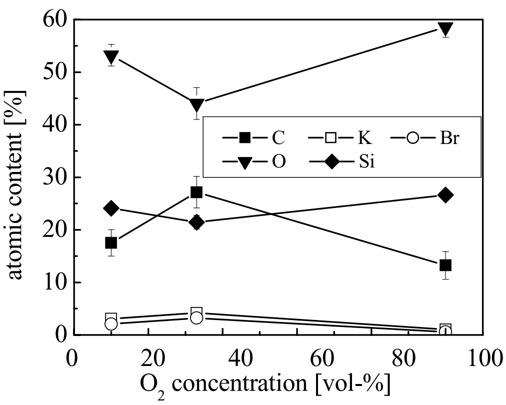

Fig. 4 Atomic content of O, Si, C, K and Br of coatings on KBr deposited in HMDSO-Ar-O_2 with different oxygen concentrations, thickness of dielectric barrier: 0.5 mm

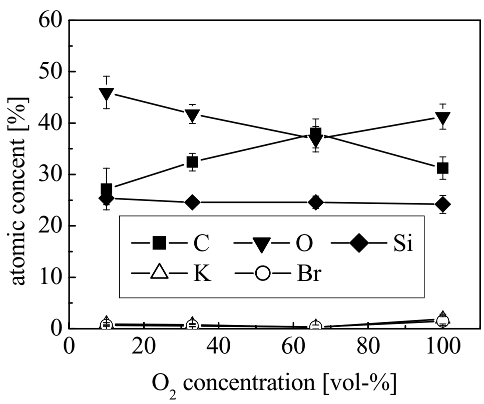

Fig. 5 Atomic content of O, Si, C, K and Br of coatings on KBr deposited in HMDSO-Ar-O_2 with different oxygen concentrations, thickness of dielectric barrier: 1 mm

With increasing discharge voltage and decreasing barrier thickness the oxygen content of the coating increases and the carbon content decreases. Increasing discharge voltage and decreasing barrier thickness have the same effect and result in increasing plasma power. Obviously, the plasma conditions play an important roll for splitting of C-Si bonds.

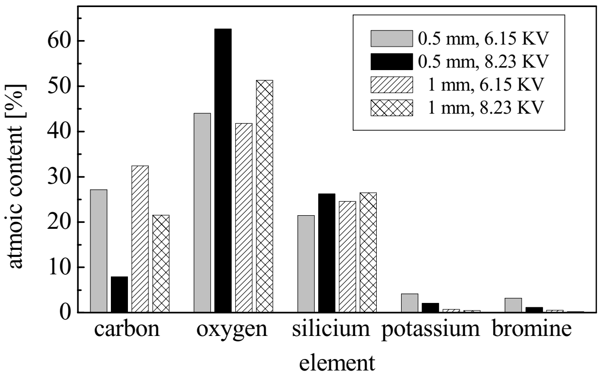

Fig. 6 Atomic content of O, Si, C, K and Br of coatings on KBr deposited in HMDSO-Ar-O_2 (33 vol.-% O_2) with different applied voltages

4. Conclusion

SiO_x containing layers have been deposited on powder particles by means of a mechanically agitated atmospheric surface discharge arrangement. NaCl and KBr powders as model substances were treated using TEOS and HMDSO precursor. The coatings completely covered the crystals.

The contents of oxygen and carbon in the deposited layer using HMDSO depend on the gas composition and the plasma power. The Si content hardly depends on Ar and O_2 concentrations in the working gas.

References

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