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High temperature stable piezoelectric, barrier and insulation coatings for sensor applications

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Abstract

The paper presents AlN, Al_2O_3, SiO_2 and Si_3N_4 films deposited by reactive magnetron sputtering at high deposition rates of 200nm/min. The deposited AlN films show a strong c-axis orientation and a piezoelectric coefficient d_{33} of 7pm/V. Al_2O_3, SiO_2 and Si_3N_4 films and their combinations are excellent insulation films on both metal and silicon substrates. High insulation strength of up to 800V was measured at room temperature and at high temperatures of 400°C. These films perform also well as barrier films. Water vapor transmission rate (WTR) of Al_2O_3 is for example 10^{-2} g/(m^2*d). Stability of the films during heat treatment at 800°C was shown. In the paper example of applications in pressure sensors and material testing are given.

Introduction

High temperature stability is a requirement on thin films for some sensor and actor applications. Requirements on the maximum use temperature vary considerably. They may range from 200°C for application in process control for injection molding, over 400…600°C for direct measurements in the combustion chamber or exhaust line of combustion engines up to 800°C for turbine applications or up to 1200°C for special heating applications.

In the paper examples of high temperature stable dielectric films deposited by reactive pulse magnetron sputtering are given. Due to the high deposition rates that can be achieved, reactive sputtering process is especially suitable for producing rather thick layers.

Required film properties are for example high breakdown field strength, high insulation resistivity, high area yield, high piezoelectric coefficient, resistance to aggressive media, a satisfactory mechanical load limit, effective permeation barriers, good adaptation of the coefficients of expansion to the substrate, dielectric strength (also in contact with electrolytes) and resistance of the layer in downstream processing steps such as laser trimming or wet-chemical etching processes. The coating costs must also be in reasonable proportion to the value of the end-product, meaning that there is often a demand for high deposition rates. The paper will not address the challenges of packaging for high temperature applications.

Deposition technology

Film deposition was carried out by stationary pulse magnetron sputtering (PMS). The Double Ring Magnetron DRM 400 of Fraunhofer-Institut für Elektronenstrahl- und Plasmatechnik (FEP) was used as the sputter source. This type of magnetron combines two concentric discharges on two separate targets in one magnetron source [1]. Film thickness uniformity of up to ±1% across an 8” wafer (200 mm) is achieved by superposition of the film thickness distributions of these two discharges (Fig. 1).

During reactive sputtering, insulating deposits on plasma shields and on the target edges may charge up and result in unwanted arcing. Therefore, pulse powering was applied in order to regularly discharge the surfaces of insulating deposits and hence ensure the long term stability of the process, even at high powers up to 10 kW. For this the pulse unit UBS-C2 (FEP) was used. This converts the dc power of two dc power supplies into current pulses for each target.

Deposition experiments were carried out by unipolar and bipolar pulse sputtering in the mid-frequency range (50 kHz) from metallic Al or Si targets. In the unipolar mode (Fig. 2a), pulse powering having negative polarity is applied between each of the targets and the common anode. This anode is not sputtered. In the bipolar mode (Fig. 2b), pulse powering with alternating polarity is applied between the two targets that act alternately as cathode and anode of the discharge. Due to the higher power at the outer target compared to the inner target, the bipolar powering is asymmetric.

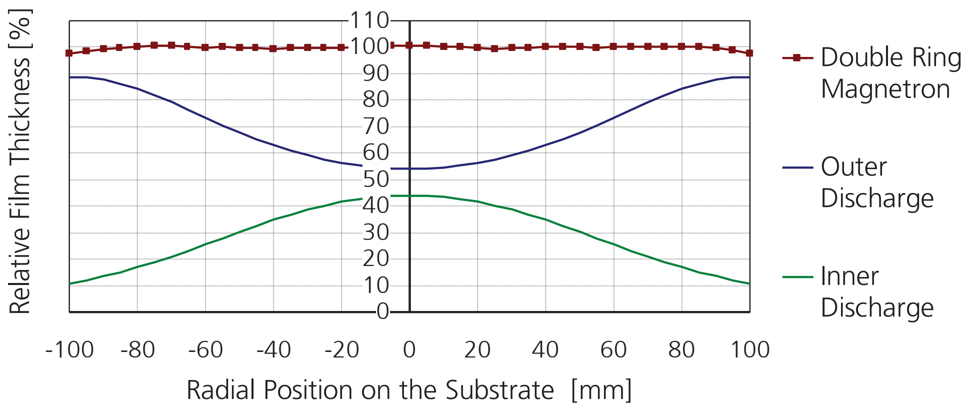

Fig. 1: Film thickness distribution across the substrate for inner and outer ring of the Double Ring Magnetron DRM 400

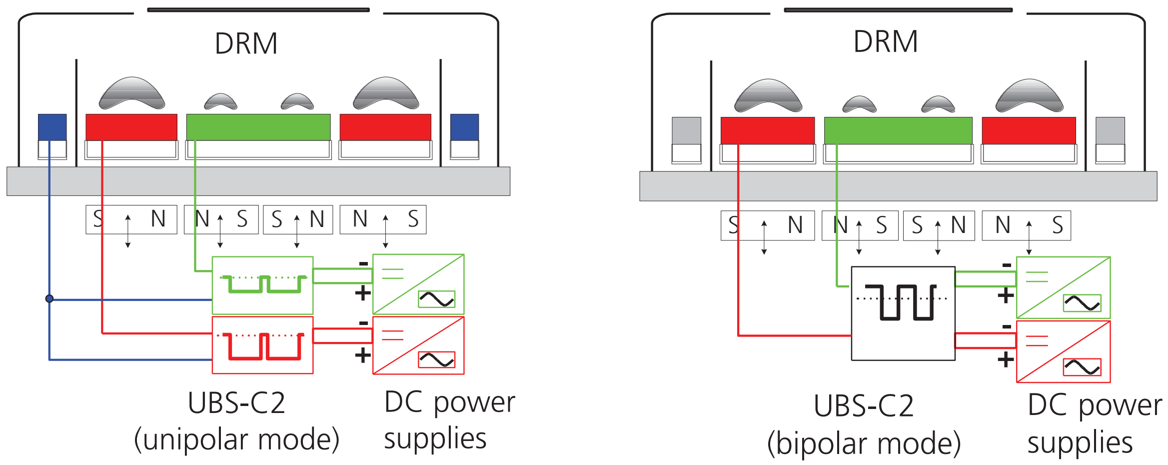

Fig. 2: Unipolar and bipolar pulsed operation of the Double Ring Magnetron

Table 1: Electron temperature and plasma density in unipolar and bipolar pulse mode, SiO_2 deposition at 7,5kW

	Electron temperature T_e	Plasma density n_e	Thermal substrate load
Unipolar pulse mode	10 eV	$1{,}8*10^{10}$ cm^{-3}	0,15 W/cm^2
Unipolar pulse mode	6 eV	$11*10^{10}$ cm^{-3}	0,75 W/cm^2

In unipolar and bipolar pulse mode here are significant differences in plasma density, electron temperature and hence energetic substrate bombardment (Table 1). In unipolar pulse mode there is an intermediate plasma density, a moderate energetic substrate bombardment and a low thermal substrate load. This is especially suitable for coating temperature sensitive substrates. In bipolar pulse mode there is a high plasma density, hence a strong energetic substrate bombardment and a high thermal substrate load. This can be used to achieve highly dense films [2].
In unipolar as well as in bipolar pulse mode closed loop reactive gas control for oxygen was applied in order to stabilize the reactive working point of the discharge in the so-called transition mode. This allows the highest possible deposition rate at a given power level to be achieved because stoichiometric films can be deposited by sputtering from a near-metallic target at high sputter yield. The SiO_2, Si_3N_4, AlN and Al_2O_3 films investigated in this paper were deposited at typically 7 kW power with deposition rates of approximately 200 nm/min for SiO_2, AlN and Al_2O_3 and 80 nm/min for Si_3N_4.

Piezoelectric AlN films

AlN films were deposited in unipolar and bipolar mode varying deposition pressure, reactive working point and the pulse parameter duty cycle. The films were investigated in the SEM concerning morphology, in the XRD concerning crystalline structure and in a d_{33} meter concerning the piezoelectric coefficient d_{33} . Results showed a strong correlation between d_{33} and the crystalline structure. Only films with an nearly pure 002 crystalline orientation showed a remarkable piezoelectric activity. Surprisingly, in both pulse modes films with strong piezoelectric activity could be achieved despite the significant differences in energetic ion bombardment of the growing film. However in both cases the parameter window for obtaining strong piezoelectric activity was very narrow and required some effort to reproduce.
Table 2 gives an overview on the film properties in both pulse modes. Fig. 3 and 4 give the XRD and SEM of AlN films deposited in bipolar pulse mode. Measurements of d_{33} in this paper were conducted at room temperature. Investigations for higher temperatures are presently carried out. Literature data suggests that piezoelectric AlN films exhibit a very use temperature of over 1000°C [3].

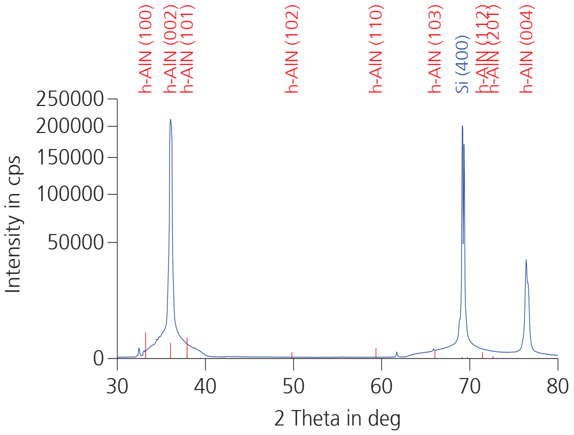

Fig 3: XRD of AlN film deposited in bipolar pulse mode

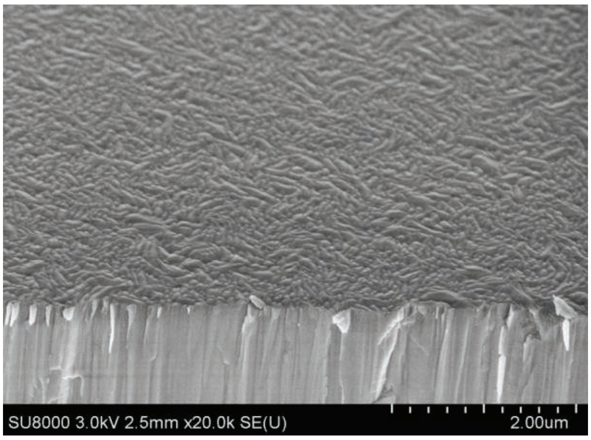

Fig 4: SEM of AlN film deposited in bipolar pulse mode

Table 2: Properties of AlN films deposited in unipolar and bipolar pulse mode

Deposition rate	3.5 nm/sec	2.5 nm/sec
Crystalline orientation	002 (99,9%)	002 (99,9%)
Density	3.16 g/cm^3	3.20 g/cm^3
Break down field strength	2.3 MV/cm	3.1 MV/cm
Resistivity	5.3 E+12 Ωcm	1.2 E+13 Ωcm
d_{33}	6.5 pm/V	7.2 pm/V
Film stress	-1 GPa	-2 GPa

Electrically insulating Al_2O_3, SiO_2 and Si_3N_4 films

Electrical insulation properties were determined by applying electrodes of 25mm^2 on top of Al_2O_3, SiO_2 and Si_3N_4 films and measuring resistivity and break down field strength between the electrode and the Si wafer. Results are given in Table 3. SiO_2 films show better insulation properties when deposited in bipolar rather then in unipolar pulse mode. Al_2O_3 film properties are slightly better in unipolar pulse mode. Si_3N_4 films show slightly inferior insulation properties compared to the other films but may be useful for example as moisture protection.
Measurements at 400°C substrate temperature were carried out by applying the same electrodes onto the steel membranes of pressure sensors. The yield during testing 50 electrodes by applying a test voltage of 250, 500 and 800V was measured at room temperature and at 400°C. Fig. 5 gives the result of these measurements. Yield at 400°C is only slightly lower then at room temperature. Surprisingly, pure SiO_2 and Al_2O_3 layers show slightly better insulating properties than the SiO_2-Si_3N_4-Al_2O_3 layer stack. We

attribute this effect to electronic defects that are present at the layer interfaces. However, the SiO_2-Si_3N_4-Al_2O_3 layer stack also fulfills the thermo -mechanical and diffusion barrier requirements.
Because of the good temperature stability the insulation layers may therefore have potential applications in automotive and aviation technology where stability at elevated temperatures is required. One example application is the direct pressure measurement in the combustion chamber of vehicle engines.

Table 3: Deposition rate and insulation properties of Al_2O_3, SiO_2 and Si_3N_4 films, measured at room temperature on silicon wafer, film thickness 1µm

Material	Pulse mode	Deposition rate [nm/min]	Resistivity [Ω*cm]	Break down field strength [MV/cm]
SiO_2	unipolar	230	$3{,}2*10^{15}$	4,3
	bipolar	150	$6{,}3*10^{16}$	5,6
Al_2O_3	unipolar	150	$2{,}3*10^{16}$	6,2
	bipolar	70	$2{,}0*10^{16}$	5,1
Si_3N_4	bipolar	80	$5{,}2*10^{13}$	2,4

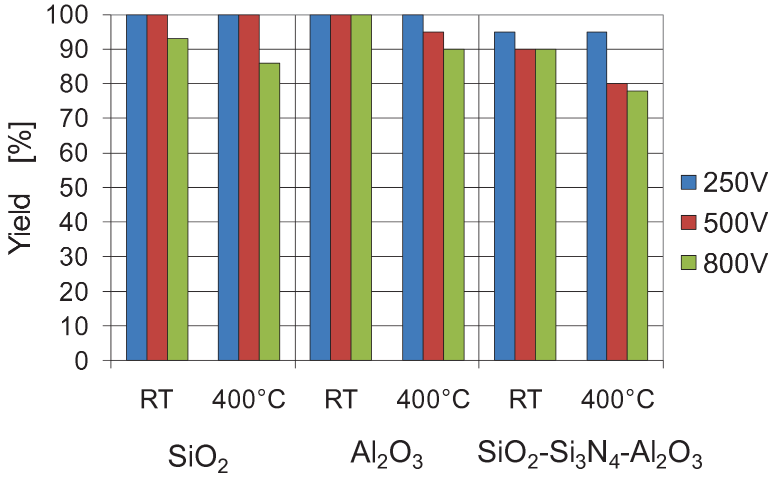

Fig. 5: Comparison of yield during testing at different probe voltages, measurement at room temperature and 400°C, steel substrate, film thickness 8µm

Besides the requirement on high operation temperature there is in some cases also the requirement on stability during following process steps at high temperature. When deposited at room temperature Al_2O_3 coatings are amorphous. If in following steps a temperature of 650°C is exceeded, the Al_2O_3 films start to become γ-crystalline. This is associated with a volume contraction and hence cracks formation in the film. Figure 6 shows for example a photo obtained by light microscopy of an Al_2O_3 film on a steel substrate after a heat treatment of 4 hours at 750°C in atmosphere.

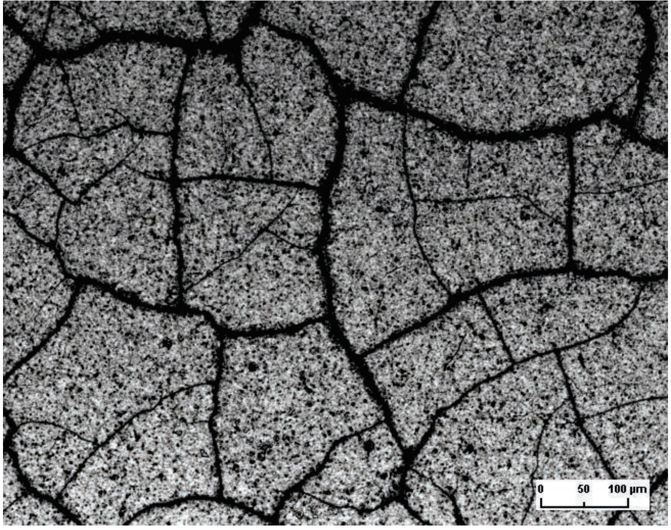

Fig 6: Light microscope photo of Al_2O_3 film on steel substrate after heat treatment of 750°C, 4h on atmosphere

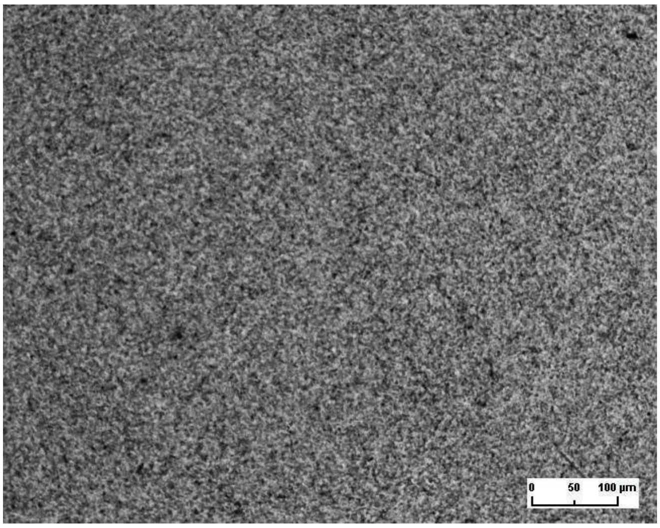

Fig 7: Light microscope photo of Al_2O_3:SiO_2(10%) film on steel substrate after heat treatment of 800°C, 4h on atmosphere

Because some applications require downstream process steps at 650…800°C it is desirable to increase crystallization temperature of Al_2O_3. During a series of experiments it was tested, whether the incorporation of a small amount of SiO_2 into the Al_2O_3 could help to rise crystallization temperature. Incorporation of SiO_2 was accomplished by the introduction of SiH_4 or HMDSO as additional process gases into the deposition chamber during reactive sputtering, by reactive co-sputtering from Al and Si targets or by using an AlSi(5%) target for reactive sputtering. With these methods Al_2O_3:SiO_2 films were obtained with an SiO_2 content varying between 4 and 10%. All of these films did not crystallize during the heat tretatment of 4 hours at 800°C in atmosphere. Figure 7 shows for example the photograph of a Al_2O_3:SiO_2(10%) after heat treatment. This film was obtained by adding HMDSO during the reactive sputtering.

Fig. 8 displays the evaluation of yield concerning electrical insulation of an Al_2O_3:SiO_2(4%) film as deposited and after the heat treatment. This film was deposited by reactive sputtering from an AlSi(5%) target. Fig. 8 shows, that the heat treatment leads to a significant reduction of yield especially at the test voltage of 800V. However, films are still good insulators.

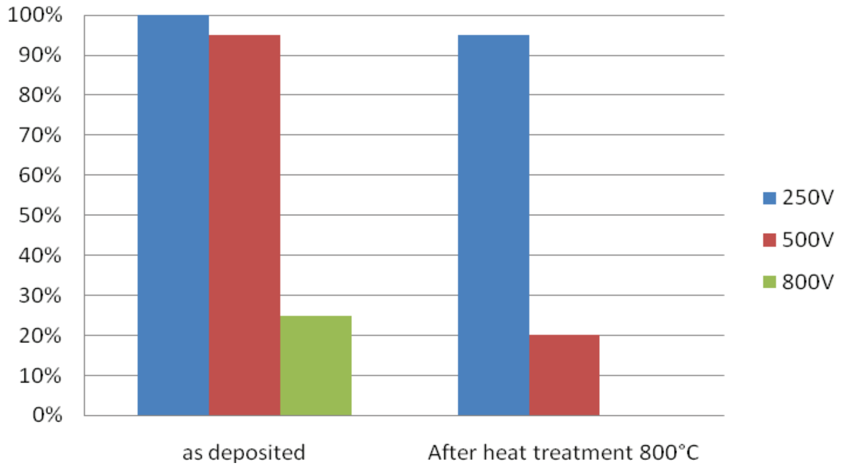

Fig. 8: Yield of Al_2O_3:SiO_2(4%) films during testing at different probe voltages, measurement at room temperature as deposited and after heat treatment at 800°C, steel substrate, film thickness 4µm

Al_2O_3, SiO_2 and Si_3N_4 as barrier films

Barrier properties were measured according to ISO 15106-03 using electrolytic method with tester WDDG of company Brugger. Measurement area was 78,5 cm^2. Table 4 gives an overview of the results. The values of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) represent the state of the art of sputtered layers on plastic web. Relevant for most applications in sensor technology however is the barrier property on rigid substrates that cannot be measured easily. Therefore from the measurements on foil no clear conclusion can be drawn which layer type and process parameter is best suited for typical sensor applications. Experience shows that especially Si_3N_4 and Al_2O_3 are good moisture barriers.

Table 4: Water vapor transmission rate (WVTR) and Oxygen transmission rate (OTR) of SiO_2, Si_3N_4 and Al_2O_3 films on 75µm PET

Material	Pulse mode	Film thickness [nm]	Water vapor transmission rate [g/m^2d]	Oxygen transmission rate [cm^3/ m^2 d bar]
PET foil			7,9	
SiO_2	unipolar	200	0,1	<0,1
SiO_2	bipolar	200	0,17	0,1
Si_3N_4	unipolar	50	0,1	0,1
Si_3N_4	bipolar	50	0,12	<0,1
Al_2O_3	unipolar	200	0,022	<0,1

Summary

Reactive sputtering allows the high rate deposition of many layer materials relevant for sensor applications. AlN films with strong 002 crystalline orientation show significant piezoelectric activity. Al_2O_3, Si_3N_4 and SiO_2 films are suitable for electrical insulation and barrier applications and show good insulation strength also at an operation temperature of 400°C. Especially Al_2O_3 is interesting for many applications because of its relatively high coefficient of thermal expansion that allows a better adaptation to the typical metal base bodies. Thermal stability of Al_2O_3 films could be significantly improved by incorporation of SiO_2. An SiO_2 content of 5..10% resulted in a shift of crystallization temperature beyond 800°C.
The good temperature resistivity of the coating makes them suitable for applications in harsh environments like combustion chambers or exhaust lines of vehicle engines or measurement in chemical industry or oil production.

References

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[3] Morito Akiyama, Toshihiro Kamohara, Kazuhiko Kano, Akihiko Teshigahara, Yukihiro Takeuchi, Nobuaki Kawahara, Advanced Materials,Volume 21, Issue 5, pages 593–596, February 2, 2009