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Spin coating of hybrid suspensions using infrared-irradiation to increase layer thickness

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ABSTRACT

This paper describes an increase in thickness of spin coated layers by using IR-irradiation. Hybrid suspensions with 5 wt.% solid content (80% $BaTiO_3$, 20% ZrO_2) are spin coated on platinized silicon wafers. The IR-irradiation increases the evaporation rate and accelerates the aging of the solution. This leads to an increase in viscosity and a faster increase of the solid content, which results in an earlier percolation of the hybrid suspension with more particles remaining on the substrate. Using IR-irradiation, an increase in layer thickness from 71 nm to 242 nm could be achieved in one coating step.

1. Introduction

1.1. Introduction

The paper is dealing with the improvement of dielectric layer thickness of $BaTiO_3$ by chemical solution deposition (CSD) via the spin coating process. An overview over CSD processes for the manufacture of oxide films can be found in [1]. These dielectric films are deposited on silicon wafers for high density integrated circuit applications, like dynamic random access memories (DRAM), cell capacitors or decoupling capacitors for multichip modules (MCM) [2–4]. The permittivity, dielectric losses, leakage currents, and the degradation behavior of the thin film capacitors are very important, e.g., for the use in DRAM or storage capacitor applications [5].

In this paper, dielectric films were fabricated via the use of hybrid suspensions which consist of two components [1,6], whose microemulsion mediated synthesis is described in [7]. One component provides a molecular precursor of ZrO_2 in solution. The other component is a nano-emulsion with nano-sized micelles which contain $BaTiO_3$ particles. Mixing of these two liquids results in the mentioned hybrid suspension, which has the potential to form core-shell structured grains in the sintered ceramic. During thermal treatment the species in the nano-sized micelles will form nano-sized grains surrounded by a shell of the species which were in molecular solution. This will improve the dielectric properties like dielectric constant and its temperature coefficient. Because the emulsion used consists of nano-sized micelles, the solid content is limited to 5 wt.%. A similar process based on microemulsions was used to produce nano-sized $BaTiO_3$ powders [7,8]. The dielectric properties of such $BaTiO_3$ coatings were investigated in [9].

The focus of the paper is the manufacture of thin films of these hybrid suspensions directly on platinized silicon wafers by spin coating. Spin coating is an easy and fast method to generate uniform thin films and is commonly used in the semiconductor industry to apply photoresist films on wafers. In spin coating of ceramic precursors the resulting films exhibit a thickness of 40–130 nm [6]. The aim of the paper is the generation of spin coated CSD-films in the thickness range between 100 and 1000 nm in one coating step.

1.2. Spin coating theory

The basic theoretical aspects of the spin coating process are described by Emslie et al. [10]. Meyerhofer et al. [11] implemented the effect of solvent evaporation into the model. Schubert et al. [12] described the spin coating process from a molecular point of view. The model as described in [10–12] can be used to calculate the thickness h as a function of time t (Eq. (1)).

$$\frac{dh}{dt} = \frac{2}{3}\frac{\rho}{\eta}\omega^2 h^3 \quad (1)$$

with ρ: density, η: viscosity and ω: angular frequency. The solution of this differential equation results in Eq. (2)

$$h = \frac{h_0}{\sqrt{1 + \frac{4}{3}\frac{\rho}{\eta}\omega^2 h_0^2 t}} \quad (2)$$

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with h_0: initial height ($t = 0$ s). Meyerhofer et al. [11] took into account a constant evaporation rate e, which leads to Eq. (3).

$$\frac{dh}{dt} = \frac{2}{3}\frac{\rho}{\eta}\omega^2 h^3 + e \tag{3}$$

This model was refined by using an iterative approach for the solution of these differential equations. This allows taking into account the time dependence of all parameters, which means they are not restricted to be constant any more. Thus it becomes possible to use time dependent values of the rotational speed, the weight loss by evaporation, the viscosity, and density, like, e.g., rpm-ramps or changes in the viscosity during the process. The iterative approach results in Eq. (4). For an accurate solution, the time-steps have to be that small that the changes within one time-step become small. For $t \rightarrow 0$ this iterative approach converges to the exact solution.

$$h_{(t_{i+1})} = \frac{h_{t_i}}{\sqrt{1 + \frac{4}{3}\frac{\rho_{(t_i)}}{\eta_{(t_i)}}\omega^2_{(t_i)} h^2_{(t_i)} \Delta t}} - e\Delta t \tag{4}$$

To achieve the desired film thickness without multiple coatings, different measures were taken to improve the layer thickness after one coating step. According to the theory, one possibility is an increase of the viscosity, which can be achieved by adding viscous components like binders, different solvents or by ageing of the hybrid suspension. Another possibility is to increase the evaporation rate, which can be realized, e.g., by temperature increase. The effect of temperature on layer thickness was studied by rising the temperature of the solution and/or of the substrate [13].

2. Experimental procedure

2.1. Materials

2.1.1. Hybrid suspension

The hybrid suspension used was synthesized by the RWTH Aachen, Germany and FZ Jülich GmbH, Germany [1,6–8]. It consists of nano-sized $BaTiO_3$ particles of about 10 nm in diameter, which constitute the center of micelles dispersed in an emulsion based on methanol as a solvent and of a dissolved molecular ZrO_2 precursor solution based on butanol as a solvent. The solid content of both liquids is currently limited to 5 wt.%. The hybrid suspension is a mixture of 80 wt.% $BaTiO_3$ emulsion and 20 wt.% ZrO_2 precursor solution, both having the same oxide concentration.

2.1.2. Wafer

To generate dielectric layers, these hybrid suspensions were directly coated on platinized silicon wafers as a substrate. The wafers of the size 10 mm × 10 mm were provided by the Institute of Electronic Materials II of the RWTH Aachen, Germany. The silicon wafer exhibits a SiO_2 layer of approx. 500 nm in thickness, followed by a thin TiO_2 intermediate layer (15 nm) and the conductive platinum top layer of approx. 100 nm in thickness.

2.1.3. Binders

To increase the viscosity, three different polyvinylbutyral binders were added to the hybrid suspension. The binders B-79 (Butvar B-79, Solutia, USA) and B-98 (Butvar B-98, Solutia, USA) exhibit a molecular weight in the range of 50,000–80,000 and 40,000–70,000, respectively. Additionally, the binder B3005 (Dolacol B3005, Zschimmer & Schwarz, GER) was used.

2.2. Spin coating

2.2.1. Coating procedure

The used spin coater (P6206, SCS Corp., USA) allows to modify the acceleration ramp, the rotational speed, the time at top speed, and the slow down ramp. The maximum rotational speed of the spin coater is 2900 rpm. The substrates are fixed to the rotary disk by means of a vacuum system. The wafer is aligned in the center of the rotary disk. Then the hybrid suspension is applied drop-wise onto the substrate until the complete surface is covered with an excess of hybrid suspension. The surface tension prevents it from spilling off the rotary disk, as long as the applied amount of hybrid suspension is not too high. Thus, three drops from a disposable pipette were applied to the wafers of 10×10 mm^2 in size. The applied volume per drop was determined in a preliminary test by gravimetry. Three drops add up to a volume of 64.4 µl ± 4.4% standard deviation. This corresponds to an average initial layer thickness of the hybrid suspension on the wafer of 644 µm ± 28 µm.

Preliminary tests were made to determine the minimum rotational speed to achieve a homogeneous coating. Suitable coatings of the 10×10 mm^2 sized wafers can be produced above rotational speeds of 1300 rpm. But the edge effects were still too large. They describe the accumulation of suspension at the wafer edge due to surface tension effects, which prevent the suspension from being spinned off. Therefore, a minimum rotation speed of 1600 rpm was used to keep the edge effects small. As a maximum 2600 rpm were used. The standard rotation speed was set to 2100 rpm.

2.2.2. Modifications by IR-irradiation

A variation of the spin coating process was developed, in order to increase the evaporation rate selectively and to change the suspension properties *in-situ*. To take this measure is not obvious from Eq. (4). By evaporation only solvent is removed, which means that the thickness is reduced without losing any solid from the rotating substrate. This means that finally less solid is removed before the film is dried. This increase in evaporation can be achieved by IR-irradiation. Therefore, the spin coater was modified. A spotlight (Concentra, 100 W 15°, Osram AG, Munich, Germany) was mounted 300 mm above the rotary disk as an IR-radiation source. The spotlight is switched on directly after applying the hybrid suspension. In order to increase the effect, a pre-evaporation step of the solvent was introduced by irradiation of the applied hybrid suspension before the rotation was started. Thereby parts of the solvent are already evaporated and the suspension becomes more concentrated. This has to be done directly on the substrate after applying the suspension. Because of this process, the hybrid suspension becomes extremely sensitive to further ageing and has to be processed immediately.

2.2.3. Sintering

Sintering was done in a muffle furnace with heaters on all six sides (LH120/12, Nabertherm, GER). A standard sinter profile was used with a maximum temperature of 800 °C (Fig. 1).

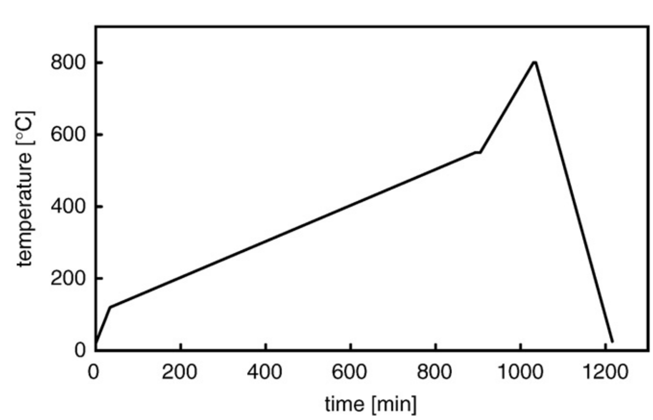

Fig. 1. Sinter profile used for thermal treatment.