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Preparation and influence of highly concentrated screen-printing inks on the development and characteristics of thick-film varistors

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Abstract

The preparation of screen-printing inks with a high solids load was studied for the development of thick-film varistors. A high solids load can ensure a higher green density of the films for enhanced densification and microstructure development in order, to obtain good current–voltage (*I–U*) characteristics for the thick-film varistor, even after short firing times at temperatures below 1000 °C. The inks with a solids load of 50, 60 and 70 wt.% enabled the preparation of thick-film varistors on an alumina substrate with a homogenous microstructure, a uniformly distributed Bi_2O_3-rich phase and a good varistor film-electrode contact after firing at 900 °C for 15 min. However, the porosity of the films gradually decreased with the increasing solids load and a varistor film prepared from the ink with the highest solids load of 70 wt.% had minimal porosity and improved *I–U* characteristics in comparison with the other samples.

Keywords: ZnO; Varistor; Thick film; Rheology; Screen printing

1. Introduction

ZnO varistors are very effective as surge and voltage protectors due to their highly non-linear current–voltage response. This non-linear characteristic originates from the electrostatic barriers at the ZnO grain boundaries that are enriched with Bi_2O_3 and highly conductive ZnO grains. The voltage at which the grain boundary becomes conductive is called the breakdown voltage. Ideally, this is at around 3 V. The breakdown voltage of a varistor is the sum of the breakdown voltages of the grain boundaries between the two electrodes and depends on the ZnO grain size and the thickness of the varistor. In order to control the ZnO grain growth, dopants such as Sb_2O_3 and TiO_2 are added. The electrical properties of the varistor ceramics below the breakdown voltage are determined by the resistivity of the grain boundaries, and above the breakdown voltage by the conductivity of the ZnO grains. To increase the conductivity of the ZnO grains, dopants such as Co_3O_4, Mn_3O_4 and NiO are added. During firing, usually at a temperature in the range from 1100 °C to 1300 °C, the complex microstructure of the varistor ceramics develops, which results in specific electrical characteristics [1,2].

For the overvoltage and surge protection of low-voltage devices, such as microelectronic circuit boards and hybrid circuits, chip or multilayer chip varistors are used as surface-mounted devices. Thick-film varistors made by the screen-printing technique open up another possibility for the integration of varistors into hybrid circuits. The possible advantages of screen printing are miniaturization, the faster and easier production of complex structures, and lower production costs. However, the screen printing of thick films has a few drawbacks, mainly because of Bi_2O_3 evaporation during firing due to a large surface-area-to-volume ratio and a strong reaction between the varistor ceramics and the substrate at the firing temperatures typical for varistor ceramics. This can be reduced by lowering the firing temperature to below 1000 °C; however, at such low firing temperatures the densification of the thick film and the development of the microstructure, required for good *I–U*

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characteristics, are hindered, even more so if the green density of the screen-printed film is low [3–7]. The problem of densification causing weak grain boundaries and a high porosity is clearly evident in the microstructure of the thick-film varistors reported in previous studies, which did not take into account the concentration of the solids load in the screen-printing ink as a key element for obtaining a high green density of the printed film [3,5,8,9]. The high porosity of the films and the hindered microstructure development can cause localization of the electrical current and, consequently, unequal heating and degradation of the varistor [2,10–12].

With the goal being to obtain as high a green density of the screen-printed thick films as possible, we studied the possibility of increasing the solids load of the varistor powder in the ink. Maintaining good printing characteristics is important for the quality of the printed film, which depends on the rheological properties of the ink. Electronic inks contain two components: a solid powder (solids load) of active material and an organic vehicle in which it is dispersed. The organic vehicle consists of solvent, polymer binder, surfactant and dispersant [8]. In terms of rheology, the inks are characterized as non-Newtonian fluids and have a shear-thinning effect as shear-dependent phenomena, which mean that the viscosity reduces with an increase in the applied stress. The shear-thinning effect originates from the ink cross-linked network that consists of inorganic particles (in our case varistor power mixture), which act as an inorganic linker, connected by the elastically active chains with sticky end groups (in our case ethyl-cellulose (EC)). The more structured is the ink network, the higher is the viscosity. The low shear causes stretching of the elastically active chains and reduces the interactions between the particles and the polymer binder. This results in free or dangling chains, producing intermolecular associations of ionic groups and coagulation of the free chains, which results in macro-agglomerates. The high shear that occurs during the passing of the ink through the mesh arranges the macro-agglomerates in the direction of the shear. This lowers the viscosity of the ink and allows it to flow through the mesh and fill the unevenness from the screen wires. After the shear is released, the free and dangling chains from the macro-agglomerates produces more junctions between the macro-agglomerates and consequently form a structured network that causes an increase in the viscosity, which in turn results in a stiff structure of the film being formed. After deposition the levelling should be slow enough to eliminate mesh imprints and quick enough to eliminate the creeping defect [13–15]. The explanations are based on the transient network theory (TNT) developed by Tanaka and Edwards [15], the application of which to the screen-printing inks was demonstrated by Sanson et al. [14].

In this study the screen-printing characteristics of concentrated inks were investigated with respect to the vehicles used and the amount of solids load using rheological and imaging methods. The rheology of the different ink compositions was characterized with a rotational viscometer using two tests: the flow test (FT) [13,16–18] and the screen-printing simulation test (SST). The SST was based on the work of Kardashian and Vellanki [16]. The printing-quality characteristics of the screen-printed thick films are discussed with respect to the rheology of the ink and the used vehicle. Printed films with a different solids load (50, 60, 65 and 70 wt.%) and the best printed quality were compared in terms of their density with SEM imaging and using *I–U* characterizations.

2. Experimental

The varistor powder mixture was prepared with a composition of 98.45 mol.% ZnO (>99.8%, Pharma 4, Grillo Zinkoxid GmbH) and 1.55 mol.% of a mixture of reagent-grade oxide powders Bi_2O_3, Sb_2O_3, Co_3O_4, Mn_3O_4, NiO, Cr_2O_3 (>99.8%). The varistor powder mixture was homogenized in absolute ethanol using a planetary mill at 200 rpm. The average particle size after homogenization d_{50} was 0.6 μm, measured with a laser-scattering particle size distribution analyser (Horiba LA-920).

The inks were prepared on a three-roll mill (EXAKT Tripple Roller Mill 50) by mixing the following constituents: varistor powder, organic vehicle, binder and, optionally, the commercially available surfactant ESL 809. The compositions of the analyzed inks are presented in Table 1 in terms of the used vehicle (the commercial vehicle and the vehicle made by ourselves) and the amounts of solids load, surfactant and binder. The proportions of the components are given with respect to the total mass of the ink.

Based on the commercial ESL vehicles, either the high-viscosity ESL CV10 or the low-viscosity ESL CV6, inks with a solids load from 50 to 70 wt.% were prepared, without (label WS) or with the surfactant (label S) ESL 809. The vehicles made by us were prepared from the solvents (2-(2-butoxyethxy) ethyl) acetate (98.4%, Merck) and α-terpineol (99.0%, Merck) in the ratio 1:4, with additions of ethyl-cellulose (EC) (ethoxyl content 48%, Acros Organics) as a binder and ESL 809 as a surfactant. Using this vehicle, three groups of inks were investigated to analyze the effect of a variation in the concentrations of the surfactant, the binder and the solids load on their screen-printing characteristics: (i) inks with a high 70 wt.% of solids load, with and without 0.6 wt.% of the surfactant (labelled as A-70S and A-70WS, respectively); (ii) inks with a 70% solids load, 0.6 wt.% of surfactant and different amounts of the binder, 2.2, 2.6 and 3.0 wt.% (labelled as A-70S, B-70S and C-70S, respectively); (iii) inks containing 65, 70 and 75 wt.% of varistor powder (labelled as B-65S, B-70S and B-75S, respectively), with 0.6 wt.% of surfactant and 2.6 wt.% of binder.

The inks' rheological properties were determined at 25 °C using a rotational viscometer, Physica MCR 301, with a cone (C25/1) and plate geometry. Two types of tests were performed to compare the properties of the prepared screen-printing inks: a flow test (FT) [13,16–18] and a screen-printing simulation test (SST) based on the reports of Lin et al. [13], Kardashian and Vellanki [16], Mezger [17] and Phair et al. [19]. In the FT the viscosity of the inks was estimated as the viscosity at shear rates ranging from the 0.01 s^{-1} to 1000 s^{-1}. From the graph of viscosity vs. shear rate the zero viscosity (η_0) and infinite viscosity (η_∞) were determined. The zero viscosity (η_0) was regarded as the viscosity measured under quasi-static conditions, i.e., at a shear rate of 0.01 s^{-1}. The infinite viscosity (η_∞) was regarded

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