PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. 2 No 1, 01NTF10(3pp) (2013)

Barium Titanate Thin Films Obtained by Screen Printing Technology

I.O. Dulina*, S.O. Umerova†, A.V. Ragulya

Frantsevich Institute for Problems of Materials Science of NASU, 3, Krzhyzhanovsky Str., 03142 Kyiv, Ukraine

(Received 19 May 2013; published online 30 August 2013)

Barium titanate thin films have been obtained using screen printing of pastes based on $BaTiO_3$ nanopowders. Obtained pastes have been characterized by optical microscopy and optical profilometry. Deposit pattern geometry fidelity in regard to screen mask and films thickness and roughness parameter Ra during screen printing parameters changing depended on pastes rheological behavior. In addition, films roughness and thickness were strongly depended on solid and solvent content in pastes. Solvent content rising and $BaTiO_3$ content lowering resulted in films thickness and roughness decreasing. Depending on paste solid and content barium titanate films thickness was changed from 1.56 to 3.18 μm, the film roughness R_a from 50 to 196 nm and R_z from 160 to 393 nm.

Keywords: Screen printing technology, Pastes, Rheological behavior, Pseudoplactic fluid, Thixotropy, Thixotropy degree, Rheopexy, Shear rate, Roughness parameter R_a, Roughness parameter R_z.

PACS numbers: 81.16.Nd, 77.55. + f

1. INTRODUCTION

The miniaturization tendency of electronic devices leads to the necessity of downsizing of multilayered ceramic capacitors simultaneously with their capacity increasing. The specific capacity of the multilayered ceramic capacitors can be increased by thickness decreasing of ceramic and electrode layers and electrodes number increasing. Thickness of metallic and dielectric layers can be decreased to 100-200 nm by using of nanosize particles and new techniques of layer manufacturing. Screen printing technology is more promising one for thin dielectric layers obtaining, but roughness, evenness and thickness of films and deposit pattern geometry are determinated by the viscosity and rheological behavior of pastes and screen printing process parameters. Thus, investigation of film characteristics dependence on screen printing pastes based on $BaTiO_3$ nanopowder composition, rheology and viscosity and screen printing process parameters of are of great importance.

2. MATERIALS AND METODS

Screen printing pastes have been prepared by using of $BaTiO_3$ nanopowder with mean particles size 20 nm, ethylcellulose as binder and terpineol as solvent.

Paste have been characterized by rheologycal viscosity analysis and printed through nylon screen with 1.5 × 2 mm patterns. Squeegee pressure range was 0.079-0.096 MPa, print and flood rates range was 0.007-0.107 m/s. Obtained films have been characterized by optical microscopy for the purpose of pattern geometry fidelity investigation and pattern relative area determination. Films thickness and roughness parameters Ra and Rz have been identified by optical profilometry.

3. RESULTS AND DISCATION

3.1 Pastes Rheological Behavior

All observed pastes had pseudoplastic behavior. Solid content increasing in pastes with invariable binder content led to raising of the paste viscosity at all shear rate range and shifting of flow curves to lower shear rate volumes. In this case flow curves shifting approached pseudoplastic pastes behavior to plastic one. In addition, thixotropy degree lowering was observed that in same cases resulted in the changing thixotropic pseudoplactic behavior in pseudoplastic and rheopexic pseudoplactic ones. Ethylcellulose content decreasing led to decreasing paste viscosity usually but sizeable viscosity increasing was observed at same solid / binder ratio in paste (Table 1). Generally it was determinated that ethylcellulose had considerable affinity to $BaTiO_3$ nanopowder: low solid content changing led to sizeable paste densifing. This leads to solid content decreasing of nanopowder in paste from 50-70 % wt.

Table 1 – Composition and rheological properties of $BaTiO_3$ pastes based on nanopowder

Paste	Components content, wt. %			Viscosity, Pa·s		Thixotropy degree, MPa/s
	$BaTiO_3$	Ethylcellulose	Terpineol	0.1 s^{-s}	500 s^{-1}	
P1	10	3	87	37.5	2.11	0.8961
P2	12.5	3	84.5	408	5.01	0.1125
P3	16.57	2.31	81.12	2780	5.94	rheopexic
P4	15.07	1.99	82.94	425	0.52	2.0280
P5	18.06	1.91	80.03	1140	0.87	rheopexic
P6	22.56	1.83	75.60	55.2	0.69	0.7608

* i_risha@online.ua
† saideshashine@mail.ru

that are typical for submicron powders to 10-15 % wt. Rheological behavior changing were associated with solid-binder structure changing in paste. At some $BaTiO_3$ / ethylcellulose ratio bonds between suspension parts are damaged, ethylcellulose molecule unrolled and all its functional groups bonded with barium titanate powder. This was attended by the changing of thixotropic pseudoplactic behavior in pseudoplastic one. In the case of rheopexic pseudoplactic pastes, possibly, each barium titanate particle bonded with the several ethylcellulose molecules and formation of 3D-structure was observed. Damaging of this structure under shear stress / shear rate increasing led to formation of disrupt bonds which generate additional paste densifing.

3.2 Patterns and Films Characterization

Deposit pattern geometry fidelity in regard to screen mask (Fig. 1) depended on paste quiescent state viscosity (shear rate 0.1 s^{-1}) and thixotropy degree (Fig. 2). Quiescent state viscosity increasing led to poor quality of deposit pattern geometry. High thixotropy degree led to viscosity increasing on the one hand and lowerind of paste printability on the other hand. Thixotropy degree lowering led to optimal squeegee pressure extending from 0.082-0.088 MPa to 0.082-0.096 MPa.

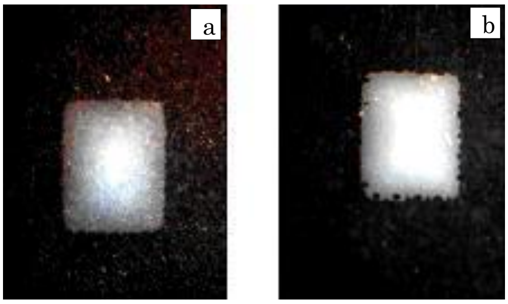

Fig. 1 – Appearance of patterns with good (a) and bad (b) geometry

Thickness and roughness parameter Ra changing under squeegee pressure increasing from 0.079 to 0.096 MPa depended on pastes rheological behavior. Squeegee pressure increasing resulted in thickness and Ra lowering for rheopexic pseudoplactic pastes and thickness and Ra changing depended on pastes binder content for thixotropic pseudoplactic ones.

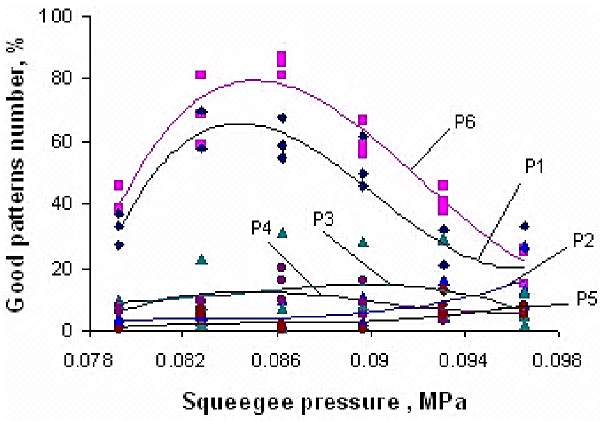

Fig. 2 – Influence of squeegee pressure on patterns number with good geometry

Squeegee pressure increasing led to thickness lowering and R_a changing had extreme behavior in case of binder content 1.8-1.9 wt. %. Thickness and R_a were invariable under squeegee pressure, print and flood rates changes for pastes binder content 3 wt. % (Fig. 3-5). The thixotropy degree depended on pattern relative area. The pattern relative area changing had extreme behavior and for optimal thixotropy degree (0.4-1 MPa/s) the relative area was 107.5-109.5 % in regard to screen mask pattern and the highest quality of deposit pattern geometry was observed.

Solid and solvent content in pastes were the main factors of films roughness and thickness. Solvent content rising and $BaTiO_3$ content lowering resulted in films thickness decreasing (Fiq. 6, 8). The roughness parameters R_a and R_z changing depended on powder and solvent content had extreme behavior but in general case solid content lowering and solvent content rising resulted in R_a and R_z decreasing (Fig. 7, 9).

Paste viscosity 2-4 Pa·s at shear rate 500 s^{-1} and thixotropy degree 0.4-1 MPa/s were considered as optimal ones for obtaining screen printed $BaTiO_3$ film with the highest quality of deposit pattern geometry and the least roughness parameters R_a and R_z.

4. CONCLUSIONS

1. Ethylcellulose considerable affinity to $BaTiO_3$ nanopowder led to sizeable paste densifing and owing

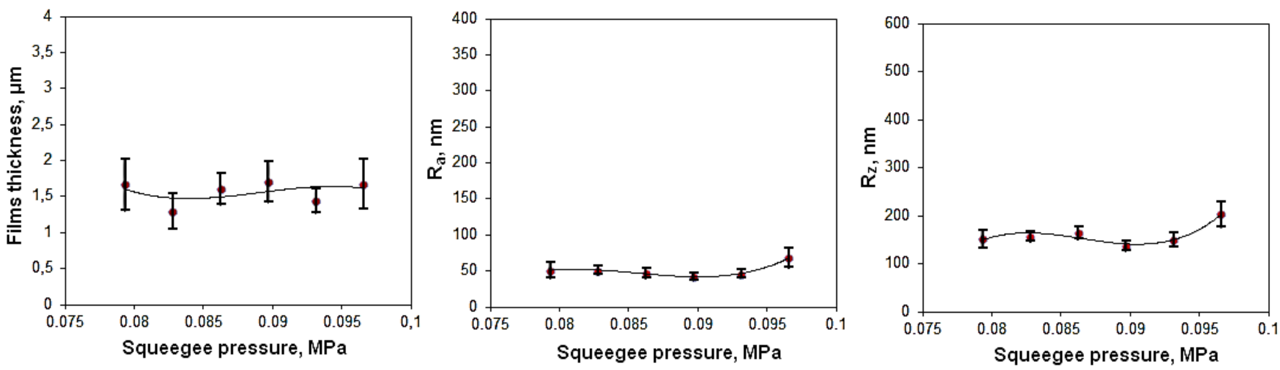

Fig. 3 – Squeegee pressure influence on films thickness and roughness for paste P1

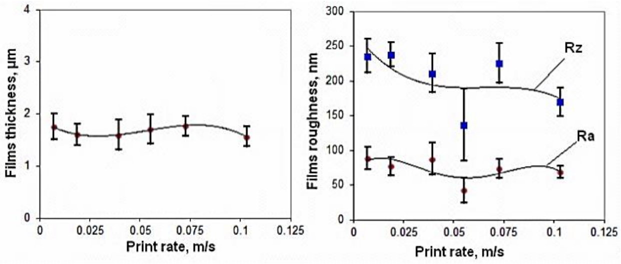

Fig. 4 – Flood rate influence on films thickness and roughness for paste P1

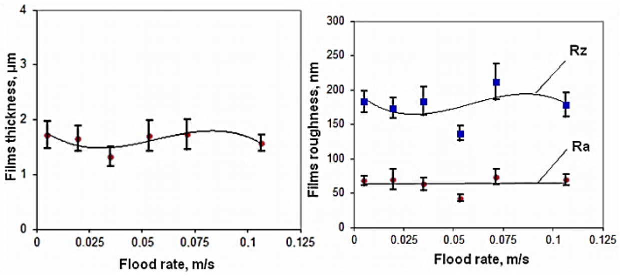

Fig. 5 – Print rate influence on films thickness and roughness for paste P1

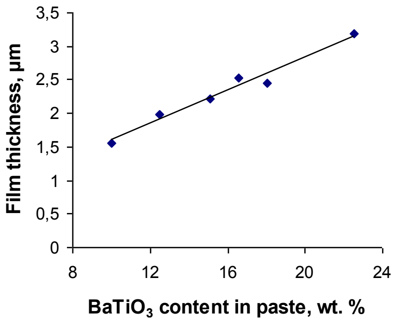

Fig. 6 – Influence of $BaTiO_3$ content on films thickness

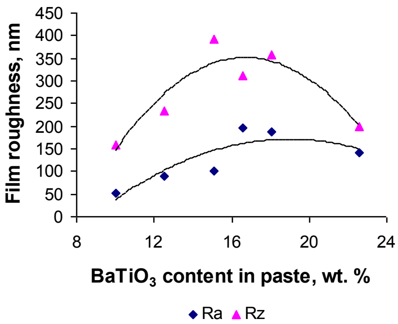

Fig. 7 – Influence of BaTiO3 content on roughness

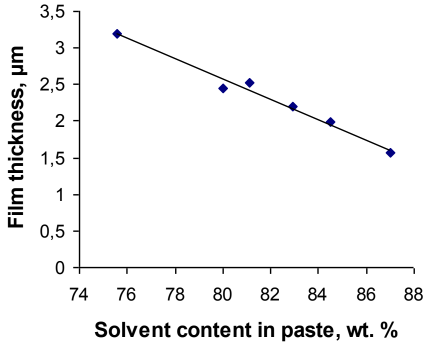

Fig. 8 – Influence of solvent content on films thickness

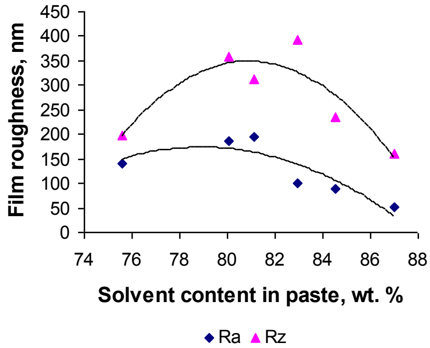

Fig. 9 – Influence of solvent content on roughness

to this paste solid content decreasing of nanopowder from 50-70 wt. % that are typical for submicron powders to 10-15 wt. %.

2. Rheological behavior changing was associated with solid-binder structure changing in paste.

3. Films thickness and roughness dependence from screen printing parameters was identified by paste rheology only in the case of paste binder content less than 3 wt. %.

4. Paste viscosity 2-4 Pa·s at shear rate 500 s^{-1} and thixotropy degree 0.4-1 MPa/s were considered as optimal ones for obtaining screen printed $BaTiO_3$ film with the highest quality of deposit pattern geometry and the least roughness parameters R_a and R_z.

AKNOWLEDGEMENTS

Authors are grateful to the State Agency on Science, Innovations and Informatization of Ukraine for a financial support for the project NN352-2012.