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The estimation of dielectric constant of thick film using Vickers indentation

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The barrier rib on plasma display panel (PDP) is a typical 3D-patterned thick film with thickness of 120 μm and it is hard to measure its dielectric constant in this state of the product. Because the porosity of ceramic thick film influenced the mechanical and dielectric characteristics, it was expected that there was the relationship between two properties. Therefore, the correlation analysis between porosity, hardness and dielectric constant of the barrier rib was studied and the exponential curve between porosity and hardness, and the quadratic curve between porosity and dielectric constant were drawn. The dielectric constant was well related to hardness by $K_{400kHz} = 0.5672 + 5.695 \ln(Hv)$.
The hardness was measured at five points on two real panels which sintered by two types of profiles and then dielectric constants and deviation were estimated by the above equation.

Key words: Ceramic thick film, Dielectric constant, Hardness, Porosity.

Introduction

Since a large-sized glass substrate over two meters has been used for manufacturing plasma display panels (PDPs), it is very important to maintain the homogeneous properties of thick film like rib and dielectric layer overall panel. Six sigma methodology, which is based on empirical and statistical data, has been used to control the materials and variables in PDP process. Even if this methodology supplies powerful solutions on the shop floor, similar troubles will occur again in the near future because this work does not explain the true cause of the problem.

Although the suppliers of materials for PDPs provide some information about their properties, users or engineers are seldom sure that materials must be distributed uniformly over the whole surface of the glass substrate. When the properties of materials are measured, the samples are small and have standard shapes. However, in real products, materials remain in thick film form with a pattern on a large substrate; with a thickness of about 120 μm and the width of about 50 μm pattern. Several standard test methods are able to measure the properties of materials with the shape of the thick film layer on glass, especially the dielectric constant. Thus, the engineers could be forced to judge the state of materials by checking the dimensions of the layer after each process and believe that the properties of the layer are the same as those provided by the supplier.

Because the barrier rib, which has three dimensional structures with narrow width and heavy thickness, plays a role in separating the red, green and blue (RGB) cells and making the space for discharging, it is intimately associated with the mis-discharging and cell defect [1]. It is difficult to explain and improve incomprehensible situations, such as mis-discharge and all-at-once cell defects by controlling the dimension of the rib. They sometimes occur without changing the raw material lot or cell dimension. It means that some unknown factor inside the rib is responsible for the variation of any properties of the thick film after sintering.

Low dielectric constant (k) materials in ultra-large scale integrated circuits are porous silica with thin and nano-patterned layers on a silicon wafer. Jain et al. studied the relationship between the dielectric constant and the mechanical properties of low-k materials using nano-indentation method, because it was hard to measure the dielectric constant of a layer with nano-thickness directly. They estimated the dielectric constant by the regression analysis among the elastic modulus, dielectric constant and porosity of materials [2]. However, the nano-indentation cannot be applied to thick film with micro scale roughness, because its impression depth is a few nanometers. Even if barrier rib has complex 3D-structure, it does simple composition of glass, alumina powder and micro-pore. Therefore, it was expected that the mechanical and dielectric properties of ribs have to be influenced by the extrinsic factor like their porosity, if secondary phases were not developed in glass or between glass and alumina.

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In this study, Vickers indentation has been used to obtain the dielectric constant of the 3D-patterned barrier rib formed in PDP, instead of nano-indentation. A regression equation was derived between the hardness and dielectric constant. The equation was used for predicting the dielectric constant of barrier ribs and its deviation on two real panels of PDP, which went through two different sintering profiles.

Experiment

The barrier rib was made by sand blast and rib materials were supplied by Daejoo Electronic Materials Co. Ltd., which were same lot (model no. DGS240S). The rib material was comprised of glass frit with Bi_2O_3-SiO_2 system (glass transition temperature of 460 °C) with 10 wt% Al_2O_3 powders.

In order to measure the dielectric constant and hardness of the rib materials, the disk-type samples ($\phi 10 \times 2$ mm) were formed using a cold isostatic press (CIP) with the pressure of 500 kgf/cm^2 (49 MPa). The LCR meter (Agilent, model: E4980A) was used to measure the dielectric constant at 400 kHz, which is adjacent to the driving frequency of PDP. Electrodes for measuring dielectric constant were printed with silver paste (Dotite, D-500) and screen print. Hardness was measured by a micro-Vickers tester (Shimadzu HMV-2), and the load was 0.2 kgf. Appearance porosity was measured by the Archimedes method with kerosene (specific gravity: 3.79 g/cm^3) instead of water. Weight of sintered samples was measured after they were saturated and suspended weight for 10 hours in kerosene in vacuum desiccator.

The correlation between porosity and the dielectric constant, as well as between porosity and Vickers hardness, was evaluated and then analyzed the relationship between the dielectric constant and Vickers hardness. The dielectric constant distribution of the rib on a real panel was estimated by the regression equation between the dielectric constant and Vickers hardness before and after changing the heat treatment conditions of the rib.

The top view of the barrier rib of the 58” FHD rear panel is shown in Fig. 1. The width of the rib was about 40 μm and the size of the cross point was about 70 μm. Because the load was 0.2 kgf in the micro-Vickers test and the size of the indentation was about 15 ~ 25 μm, the cross point was selected to measure the hardness of real panels. The hardness data was obtained from 5 locations per panel and 15 points per location.

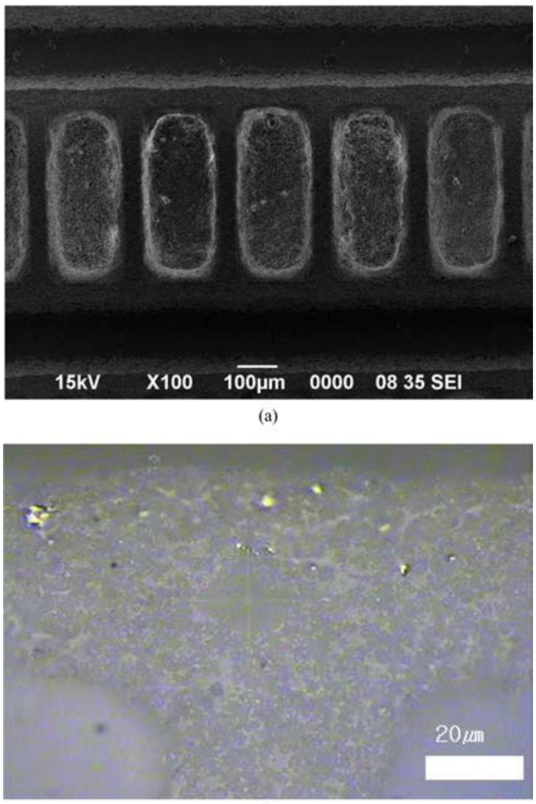

Fig. 1. The top view of barrier ribs of a 58-inch FHD TV rear panel, (a) SEM image and (b) microscope image with Vickers indentation.

Results and Discussion

Fig. 2 shows the contour plot of porosity versus firing temperature and duration time. The porosity decreased rapidly with temperature and duration time to reach the minimum value in 30 minutes at the lowest temperature, 530 °C. The densification of glass powder is not related to the solid state sintering process but rather to the viscous flow of glass (Mckenzie-Shuttleworth model) [3]. The M-S model explains the final step in the vitrification of glass powders, in which the body with frits is densified by the softening of glass powders, and pores are trapped inside. The microstructures of cross sections of rib s in Fig. 3 show that a firing temperature over 550 °C induces the final sintering stage with closed pores. The microstructure with closed pores was similar to the model of low-k materials, therefore it was expected that the method of Jain et al. could be applied to obtain

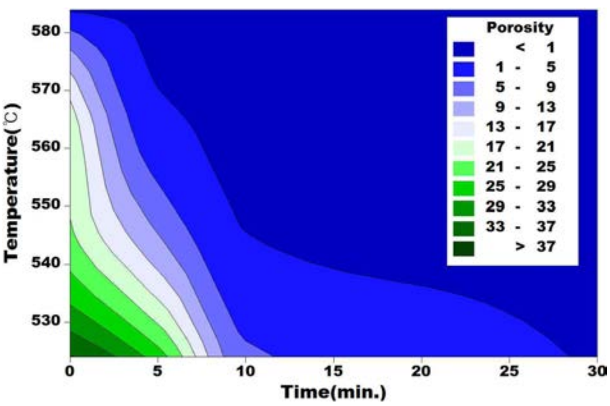

Fig. 2. The contour plot of porosity versus firing temperature and time.

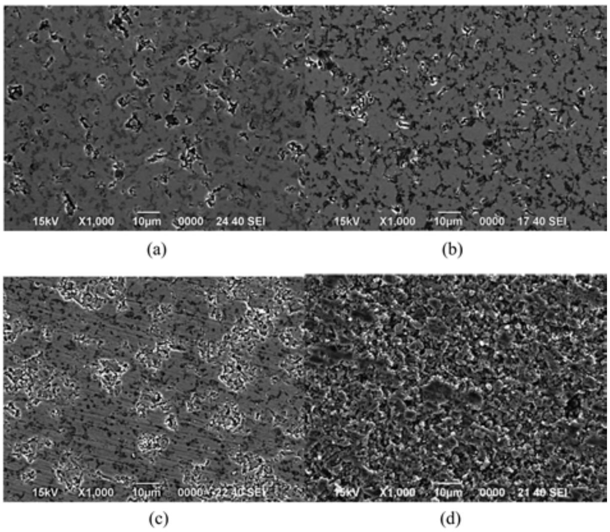

Fig. 3. The microstructures of cross sections of ribs with different porosity, (a) 0.52%, (b) 7.17%, (c) 12.10%, (d) 26.48%.

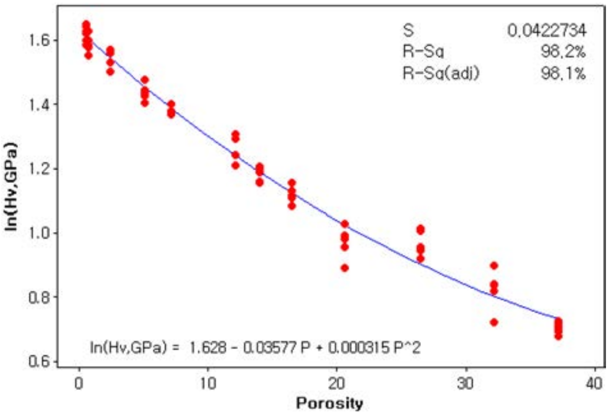

Fig. 4. The relationship between hardness and porosity.

the dielectric constant of the barrier-rib-patterned thick film for the PDP. On the other hand, fast vitrification over 580 °C without holding time is proposed to improve the firing condition for productivity.

Fig. 4 shows the changes of hardness and dielectric constant with porosity. Equation (1) or (2) could be obtained from curve fitting between hardness and porosity.

$$\ln(Hv) = 1.585 - 0.02496\ P\ (R^2(adj.) = 96.5\%) \qquad (1)$$

$$\ln(Hv) = 1.628 - 0.03577\ P + 0.000315\ P^2\ (R^2(adj.) = 98.1\%) \qquad (2)$$

where, Hv is the Vickers hardness (GPa) and P is the porosity.

McColm described how the hardness of tetragonal zirconia decreases as an exponential function of porosity [4]. Luo et al. also found that the hardness of 3Y-TZP had has an exponential relationship with porosity, as well as its elastic modulus and obtained an equation similar to equation (1) [5]. Because commercial software (Minitab res. 15) was used for curve fitting and R^2(adj) in equation (2) was higher than in equation (1), it was considered that equation (2) was more adequate to present the relationship between the porosity and hardness of sintered barrier rib samples.

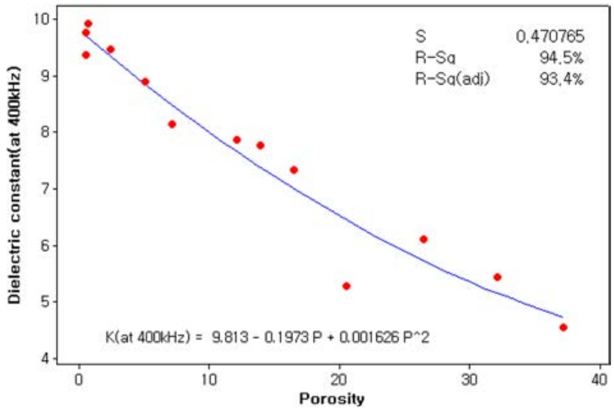

Fig. 5. The relationship between dielectric constant and porosity

The relationship between porosity and dielectric constant is shown in Fig. 5. The dielectric constant decreased with porosity, and equations (3) or (4) explain the relationship between two properties. Previous studies [6-9] suggest the non-linearity between the dielectric constant and porosity. Rust et al. induced the regression equation on the dielectric constant and porosity of volcanic rocks using the Lichtenecker and Rother equation (L-R eq.), which is related to the theory of mixing two materials; $K_T^{\alpha} = \Sigma\Theta_i K_i^{\alpha}$, where K_T is the total dielectric constant, Θ_i and K_i are the volume fraction and dielectric constant of i components (e.g., pores and solids), and α is a geometric factor. The equation by Rust was close to linear because α is 96%. It is very close to the theoretical upper limit ($\alpha = 1$) which is strictly linear. Linear indicates the arrangement of columns of solid and air perpendicular to the electrodes. Clearly, this is not an accurate description of pore geometry. They suggested that, if pore size is larger than (or of similar dimensions to) the sample thickness, then the geometry in the sample may be approaching to a parallel arrangement at high porosity [7]. In this study, the fitted line between the dielectric constant and porosity deviated slightly from the linear line, so geometry in the sample could be considered a parallel arrangement at high porosity. However, micro-structure with low porosity (Fig. 3) had isolated pores, which induced non-linearity.

$$K_{400kHz} = 9.813 - 0.1973\ P + 0.001626\ P^2\ (R^2(adj) = 93.4\%) \qquad (3)$$

$$K_{400kHz} = 9.590 - 0.1415\ P\ (R^2(adj) = 92.5\%) \qquad (4)$$

Figs. 4 and 5 and equations (2) and (3) indicate that there is the relationship between the dielectric constant and Vickers hardness (GPa); the regression equation (5) and Fig. 6 could be induced. Though Jain et al. suggested that there is a linear relationship between mechanical property and dielectric constant

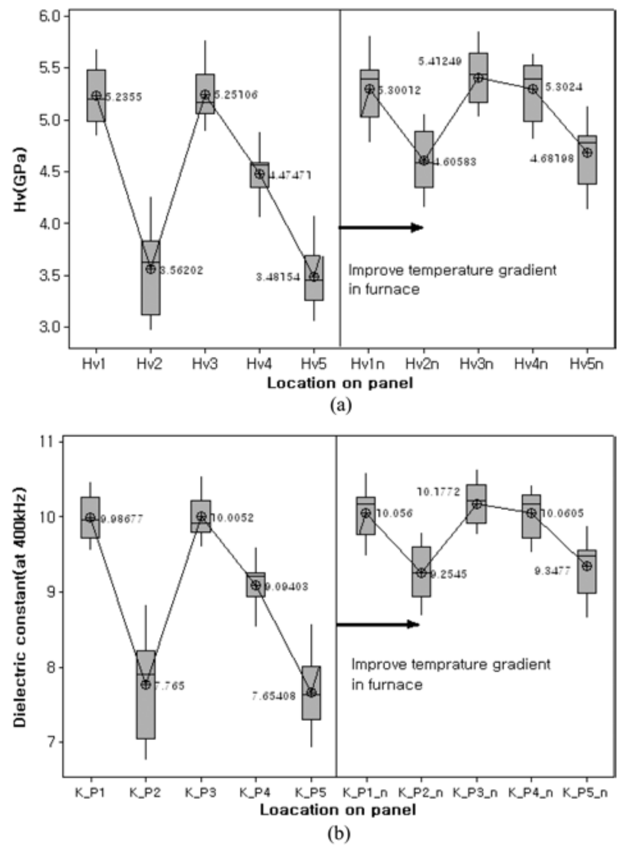

Fig. 6. The relationship between dielectric constant and hardness.

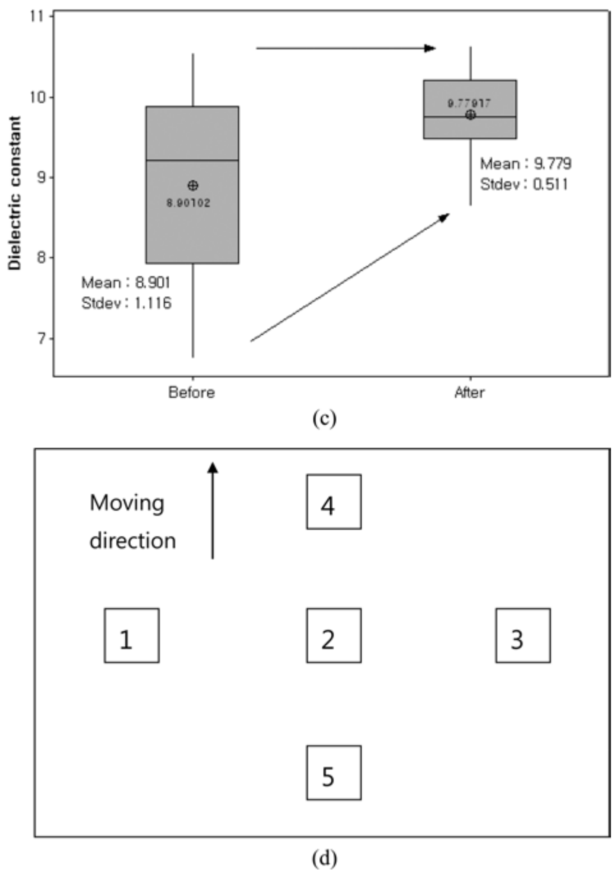

Fig. 7. The change of hardness and dielectric constant of real panels before and after improving different temperature gradients in the sintering process: (a) hardness, (b) dielectric constant according to location, (c) deviation of dielectric constant, and (d) sampling location and moving direction of the panel.

[2], equation (5) was only slightly nonlinear, as shown in Fig. 6. Nevertheless, it was considered that equation (5) will be used to estimate the dielectric constant from the Vickers hardness, because the fitting curve was close to linear below the dielectric constant of 9. Thus, the dielectric constant of thick film could be obtained from micro-Vickers indentation instead of nano-indentation which is applied on thin film by Jain.

$$K_{400kHz} = 0.5672 + 5.695 \ln(Hv)\ (R^2(adj) = 96.0\%) \quad (5)$$

Fig. 7 (a), (b) and (c) show the dielectric constant distribution of the rib on a real panel using equation (5) before and after the heat treatment condition is changed. The hardness of the rib at the substrate side (positions 1 and 3) was higher than in the center (positions 2, 4, and 5), which means that the dielectric constant of the side is higher than that of the center. There was a serious temperature gradient perpendicular to the glass moving direction before the change of heat treatment condition, which could lead to the deviation of dielectric constant and mis-discharge all over the panel. Even if the deviation of dielectric constant existed slightly after the adjustment of the furnace temperature gradient, the deviation of dielectric constant could be decreased.

Conclusions

In this work, the dielectric constant of barrier rib coated on glass plate for PDP was estimated using its hardness. As the mechanical and dielectric characteristics were known to depend on the porosity of various ceramics, the above relationship of the barrier rib with PDP as the typical thick film was checked. The exponential relationship between porosity and hardness and the non-linear curve between porosity and the dielectric constant were drawn. The exponential equation could be derived between dielectric constant and hardness.

Measurement of the thick film on a real panel and control of the quality of the thick film in a real manufacturing process can be performed using the previous equation and method.

Acknowledgements

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