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*Flexible white OLED (organic light emitting diode) is a subject of intense research due to its application as versatile lightings for housing and flexible backlight unit for TFT-LCD. In order to make flexible OLED, flexible transparent conductor substrate is required which can replace ITO-glass used in current OLED devices. Another important point is a good gas barrier property of the flexible ITO-film, since the water vapor transmission rate (WVTR) of polymer film is much higher than that of ITO-glass and the life time of OLED device is very sensitive to the transmitted water vapor. In this work, a wet process of forming gas barrier layer on polyethersulfone (PES) film was studied utilizing spin coating of polysilazane solution and thermal conversion to thin $SiO_2$ barrier layer. The flexible white OLED fabricated with this ITO-$SiO_2$ (polysilazane)-PES substrate exhibited about equal power and current efficiencies to the OLED made with ITO-glass.*

**Keywords:** flexible OLED; gas barrier; OLED; polysilazane

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## INTRODUCTION

Organic light-emitting diode (OLED) has been developed rapidly for application to the mobile displays such as car navigator, PMP, and game displays. In the near future flexible displays based on OLED are also expected to be introduced in the market [1–3]. OLED devices fabricated on the plastic substrates, such as PES, have merit of thin and lightweight displays in addition to new design capability [4–6].

Among the plastic substrates, PES has been widely tested in the OLED devices owing to its low cost and good mechanical properties [7]. However, OLED devices fabricated on PES substrate exhibited limited life time due to high diffusion rate of water vapor and oxygen through the plastic substrate compared to glass substrate. In order to decrease the penetration of water vapor and oxygen, thin inorganic barrier films were deposited on the plastic substrate by various methods including RF magnetron sputtering, electron beam evaporation and plasma enhanced chemical vapor deposition (PECVD) [8–10]. The degree of gas transmission depends on plastic substrate thickness, permeating gas, and barrier film quality. Roberts et al. proposed a model for gas permeation into inorganic oxide coated gas barrier films which was based on three different transport mechanisms; hindered transport through the amorphous lattice (interstice $\sim$0.3 nm), hindered transport through 'nano-defects' (interstice $\sim$1 nm) and unhindered transport through 'macro-defects' (interstice $>$1 nm). Gas permeation is considered to be defect-dominated [11–13].

In this work, we studied the formation of gas barrier layer by using polysilazane coating followed by thermal conversion to $SiO_2$ layer and its effect on the electro-optical properties of OLED devices.

## EXPERIMENTAL

### Materials

PES film used as flexible substrate was purchased from i-Component Co. in Korea and polysilazane solution was from AZ Electric Material Co. in Japan. The OLED materials 4,4′-bis(2,2-diphenyl-ethen-1-yl) dipheyl [DPVBi] used as blue host, red dopant 4-(Dicyanome thylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljuloidin-4-yl-vinyl)-4H-pyran [DCJTB], green dopant 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H-5H-11H-10-(2-benzothiazoly)quinolizino-(9,9a,1gh)coumarin [C545T] and hole transport agent [NPB] were purchased from Lumtec Co.

Electron transport agent [BCP] was obtained from Doosan Co. in Korea and lithium floride [LiF] from Aldrich Chemical Co. and aluminum [Al] from High Purity Chemical Laboratory Co.

## Formation of Gas Barrier Layer with Polysilazane

Polysilazane solution was spin coated on the PES film ($50 \times 50\,mm^2$, thickness 200 μm). The substrate was dried in the convection oven at 120°C for 1 hr. The dried polysilazane film was then heat treated at 100°C for 3 hr under 85% relative humidity to convert polysilazane to inorganic thin film of $SiO_2$ (thickness 150 nm).

## ITO Thin Film Deposition

Indium tin oxide (ITO) thin film was deposited on top of the $SiO_2$ gas barrier formed PES film utilizing low frequency (60 Hz) magnetron sputter. A typical deposition condition was LF power 320 volt, Ar gas flow rate of 30 sccm, distance from ITO target to substrate 100 mm, deposition time 10–20 min under room temperature.

## Fabrication of White OLED Device

White OLED devices were fabricated as follows. First, polysilazane solution was spin coated on the PES film and then heat treated as described in the formation of gas barrier layer session. Deposition of ITO on top of this substrate gave about 150 nm thick ITO layer on top of the $SiO_2$ gas barrier coated PES film. Thermal deposition of hole transport layer (NPB, 45 nm), light emission layer (DPVBi + DCJTB, 30 nm), electron transport hole blocking layer (BCP, 40 nm) followed by electron injection layer (LiF, 0.5 nm) and aluminum cathode (150 nm) gave white OLED as shown in Figure 1.

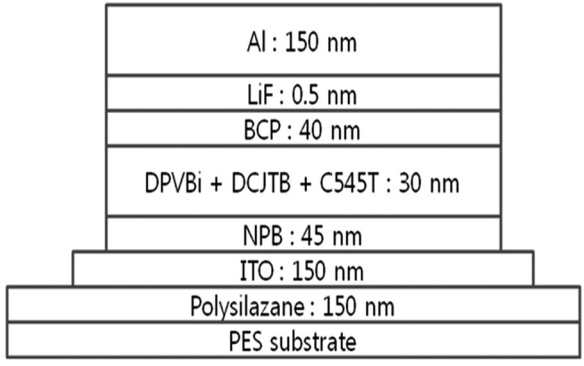



**FIGURE 1** Structure of white OLED device on PES substrate.

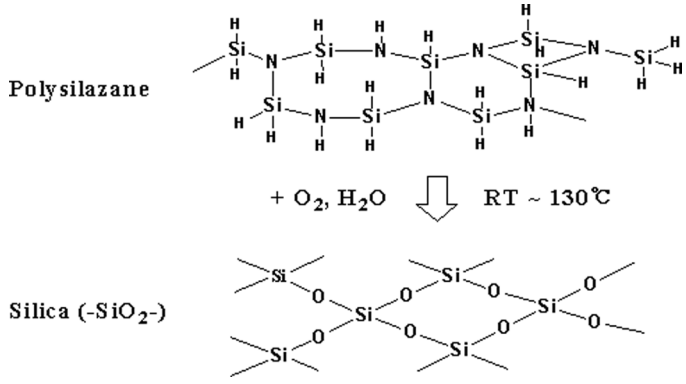
## Measurements

Infrared spectra were obtained with a JASCO FT-IR 620 spectrometer. UV-visible absorption and photoluminescence spectra were measured on a JASCO V-650 spectrometer and JASCO FP-6500 fluorescence spectrometer, respectively. The ionization potential of organic materials were obtained with atmospheric photoelectron spectroscopy (Riken Keiki AC-2). Electroluminance (EC) spectra, color coordinates and other electro-optical properties were measured by using Spectroscan PR-650 (Photoresearch Inc.) equipped with Kiethley 2400. The sheet resistance of ITO layer was measured by Loresta-EP four point probe (Mitsubishi Chemical Co.). The WVTR was measured with Permatran-W (Mocon Co.) at 37.8°C for 37 hr.

## RESULTS AND DISCUSSION

### Property of $SiO_2$ Gas Barrier from Polysilazane Coating

Polysilazane is a unique material which can be converted from polymer film to inorganic $SiO_2$ thin film by the thermal treatment under the presence of air and water vapor (100°C, 85% RH, 3 hr). The reaction procedure is shown in Scheme 1. The condition of thermal treatment was followed by FT-IR spectrometry. Figure 1 shows the FT-IR spectra of polysilazane film according to the thermal treatment. It was found that the polysilazane peaks (Si-H at 2156 $cm^{-1}$, N-H at 3370 $cm^{-1}$ and 1176 $cm^{-1}$, Si-N at 844 $cm^{-1}$) before thermal conversion all disappeared and new peaks from inorganic $SiO_2$ thin film (Si-O-Si at 1072 $cm^{-1}$ and 451 $cm^{-1}$) were observed after thermal conversion.




**SCHEME 1** Thermal conversion process of polysilazane film.

The thickness and surface roughness of the thermally converted $SiO_2$ thin film from polysilazane coating were analyzed according to the initial spin coating condition of polysilazane solution as shown in Table 1. The surface uniformity of the thermally converted $SiO_2$ thin film was best at the spin coating speed of 1,500 rpm (two times) which gave 150 nm thickness of $SiO_2$ after initial drying (120°C, 1 hr) and thermal conversion(100°C, 85% RH, 3 hr). It was also noted that the surface roughness of the converted $SiO_2$ film (0.557 nm RMS) was better than that of PES bare film (3.400 nm RMS) as shown in the SEM photographs in Figure 2.

The gas barrier property of the $SiO_2$ thin film converted from polysilazane is shown in Table 2. Polysilazane solution was spin coated to give three different thickness of $SiO_2$ film after thermal conversion. The water vapor barrier property of $SiO_2$ thin film was improved from 53.3 $g/m^2$/day (bare PES film) to 0.81 $g/m^2$/day ($SiO_2$/PES film). The $O_2$ gas barrier property was improved to 8,000 times from the bare PES film. When the $SiO_2$ barrier layer converted from polysilazane film was thicker than 150 nm, the $H_2O$ or $O_2$ barrier property were not improved but deteriorated. This might be caused by the imperfect conversion of thick polysilazane layer which would lead to segregated domain formation. When comparing $SiO_2$ barrier layer film was deposited onto the PES film by RF magnetron sputtering with multiple $SiO_2$ layer formed by sputtering and polysilazane coating, the multiple coating of $SiO_2$ by polysilazane and $SiO_2$ sputtering gave about two times better water vapor barrier property as shown in Table 3.

**TABLE 1** Physical Property of $SiO_2$ Gas Barrier Layer Obtained by Polysilazane Coating and Thermal Conversion

| | Spin coater condition | | | | | Physical property | |
|---|---|---|---|---|---|---|---|
| | 1-Step | | 2-Step | | | | |
| Sample No. | Rate (rpm) | Time (sec) | Rate (rpm) | Time (sec) | Curing condition | Thickness | Surface roughness (RMS:nm) |
| 1 | 800 | 10 | 1500 | 10 | 1hr at 120°C → 3hr at 100°C/ 85% RH | 9.76 μm | 7.48 |
| 2 | 1000 | 10 | 1500 | 10 | | 3.24 μm | 5.26 |
| 3 | 1000 | 10 | 2000 | 10 | | 2.56 μm | 3.56 |
| 4 | 1500 | 10 | 1500 | 10 | | 150 nm | 0.557 |
| 5 | 2000 | 10 | 2000 | 10 | | 100 nm | 0.869 |
| 6 | 2000 | 10 | 2500 | 10 | | 80 nm | 1.32 |
| 7 | 2500 | 10 | 3000 | 10 | | 75 nm | 1.57 |
| 8 | 3000 | 10 | 3000 | 10 | | 65 nm | 2.74 |
| Bare PES | – | | | | | – | 3.40 |

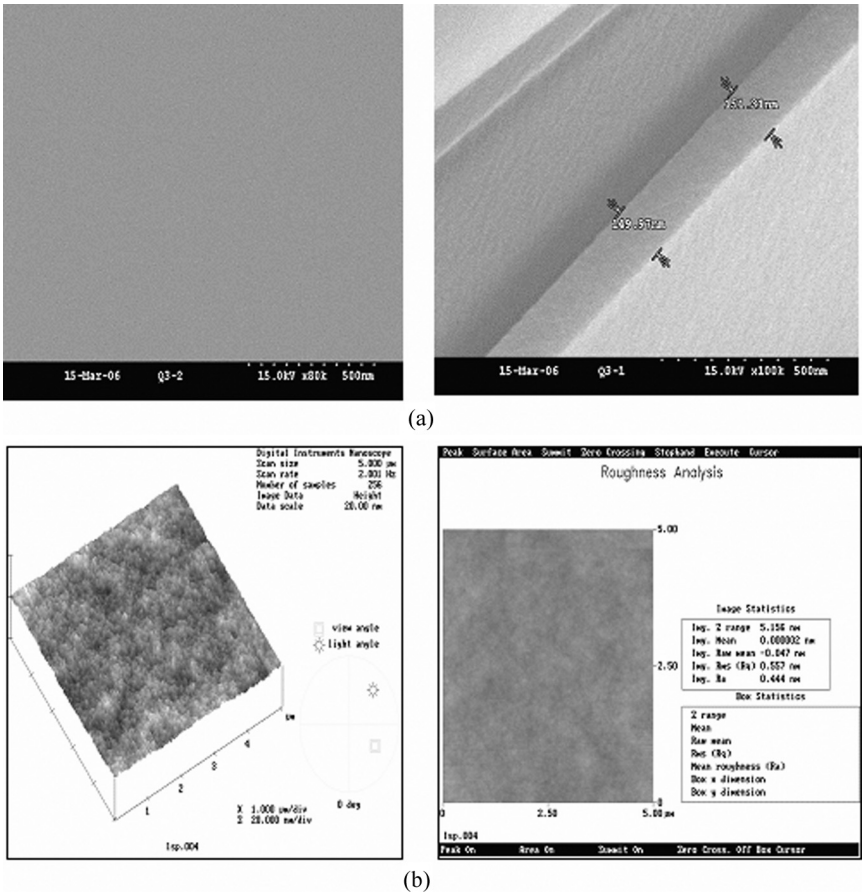



**FIGURE 2** Thickness and surface photographs of $SiO_2$ thin film on PES obtained from polysilazane coating and thermal conversion: (a) thickness, (b) surface roughness.

**TABLE 2** Water Vapor and Oxygen Transmission Rate vs. Thickness of $SiO_2$ Gas Barrier Layer Converted from Polysilazane

| No. | $SiO_2$ film thickness | WVTR ($g/m^2/day$) | OTR ($cc/m^2/day$) |
|---|---|---|---|
| 1 | 9.76 μm | 0.87 | 0.041 |
| 2 | 3.24 μm | 0.72 | 0.035 |
| 4 | 150 nm | 0.81 | 0.024 |
| Bare PES | – | 53.3 | 253 |

**TABLE 3** Gas Barrier Property of PES Film and Gas Barrier Formed PES Films

| PES films with gas barrier | Water vapor transmission rate ($g/m^2 \cdot day$) |
|---|---|
| Bare PES | 53.3 |
| $SiO_2$ (10 nm)/PES | 1.1 |
| $SiO_2$ (20 nm)/PES | 0.88 |
| Polysilazane → $SiO_2$ (150 nm)/PES | 0.72 |
| Polysilazane → $SiO_2$ (150 nm)/$SiO_2$ (20 nm)/PES | 0.45 |

**TABLE 4** Sputtering Condition of ITO and Physical Properties

| | Sputtering condition | | | | Physical and electric property | |
|---|---|---|---|---|---|---|
| No. | Deposition time (min) | LF power (V) | Temp. | Ar gas (SCCM) | Thickness (nm) | Surface resistance ($\Omega/\square$) |
| 1 | 10 | 320 | RT | 30 | 120 | 90 |
| 2 | 15 | 320 | RT | 30 | 150 | 80 |
| 3 | 17 | 320 | RT | 30 | 180 | 80 |
| 4 | 20 | 320 | RT | 30 | 215 | 60 |

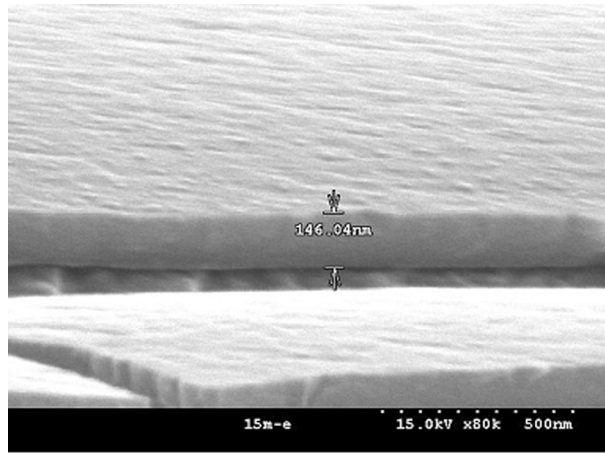



**FIGURE 3** SEM photographs of ITO layer deposited on PES film.

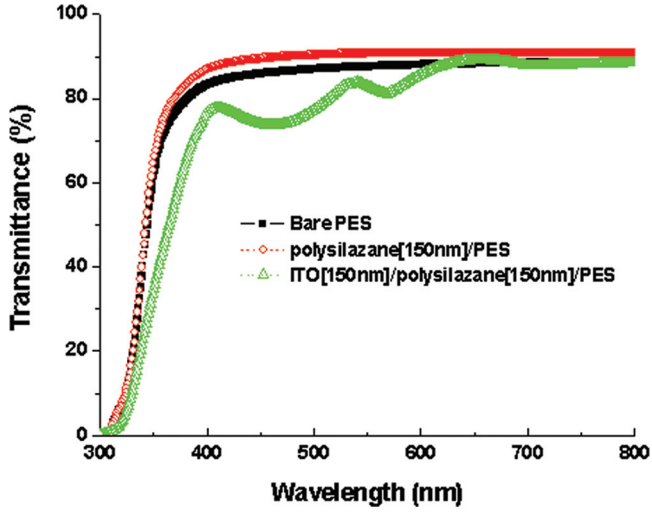



**FIGURE 4** Transmittance of various PES films.

## ITO Deposition on $SiO_2$-PES Film

ITO coated polymer film is used as the transparent conductor substrate for the fabrication of flexible display based on OLED device system. The performance of ITO coated PES film on which $SiO_2$ gas barrier

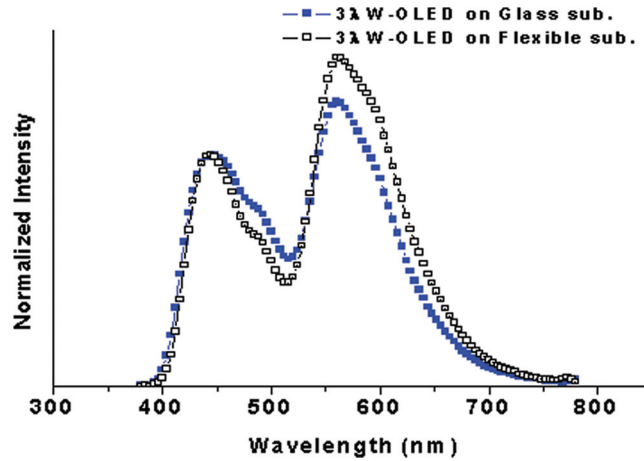



**FIGURE 5** EL spectra of white OLEDs fabricated on glass and flexible substrate.

**TABLE 5** Characteristics of Flexible White OLED Fabricated on ITO Glass and ITO Film with Gas Barrier Layer

| Concentration (wt.%) | | | Max luminance/voltage | | Max power/current efficiency | | | Color coordinate turn on voltage/max voltage | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OLED Device | DCJTB | C545T | $cd/m^2$ | V | lm/W | cd/A | Turn on voltage | X | Y | X | Y |
| Glass | 0.060 | 0.008 | 11,500 | 12 | 1.1 | 3.1 | 5 | 0.3290 | 0.3453 | 0.3249 | 0.3406 |
| Plastic | 0.060 | 0.008 | 1,100 | 13 | 1.0 | 3.3 | 7 | 0.4391 | 0.4506 | 0.3551 | 0.3551 |

was formed from the polysilazane varied widely according to the low frequency (60 Hz) magnetron sputtering condition of ITO as shown in Table 4. The sheet resistance of ITO-$SiO_2$-PES film on which ITO layer was about 150 nm as shown in Figure 3 was 80 $\Omega/\square$ compared to $20 \sim 50$ $\Omega/\square$ of ITO glass used in OLED device fabrication.

The reason for this high sheet resistance was that the surface uniformity of PES substrate was not as good as that of polished glass and the deposition temperature of ITO was lower than that of ITO glass.

The transmittance of ITO-$SiO_2$-PES film is shown in Figure 4 with the bare PES and $SiO_2$ (polysilazane)-PES film in the visible region.

The transmittance of ITO-$SiO_2$-PES was 83% compared to 90% of the $SiO_2$ (polysilazane)-PES film. The reason for decreased transmittance seemed to be the different refractive index of the ITO (2.00), $SiO_2$ (1.40) layer and PES (1.65) film.

## Performance of White OLED Fabricated on ITO-$SiO_2$-PES Substrate

White OLED devices based on 3-wave method were fabricated both on the ITO-$SiO_2$ (polysilazane)-PES flexible substrate and ITO-glass. The ratio of the emitting materials were DPVBi/DCJTB/C545T = 99.932/0.06/0.008 wt.% which was prepared in powder form in advanced by making emitting materials solution in this ratio and then complete evaporation of the solvent. This emitting materials were deposited on top of the hole transport layer (NPB) followed by electron transport (LiF) layer and Al cathode as described in the experimental session.

The EL spectra of white OLED made on ITO glass and ITO-$SiO_2$ (polysilazane)-PES substrate are shown in Figure 5. The performances of both rigid and flexible white OLEDs are summerized in Table 5. The maximum luminance of rigid and flexible white OLED was 11,500 cd/$m^2$ and 1,100 cd/$m^2$, respectively. However the power and current efficiency of the two devices were 1.1 lm/W, 3.1 cd/A and 1.0 lm/W, 3.3 cd/A, respectively. These results indicated that the main reason for the low luminance of flexible OLED device is low current density, that is high sheet resistance of ITO-$SiO_2$ (polysilazane)-PES substrate as described earlier in the ITO deposition part.

## CONCLUSIONS

Thin inorganic gas barrier layer ($SiO_2$) was formed on PES film by spin coating of polysilazane solution, drying and thermal conversion for 3 hr under the condition of 120°C, 85% RH. The WVTR of $SiO_2$ (150 nm)-PES film was reduced to 0.81 g/$m^2$/day from 53.3 g/$m^2$/day

of PES bare film. The surface roughness of bare PES film (3.40 nm RMS) was improved to 0.557 nm (RMS) with the $SiO_2$ (polysilazane)-PES film.

ITO thin film was deposited on the $SiO_2$ (polysilazane)-PES film by low frequency 60 Hz) magnetron sputtering method utilizing $SiO_2$ target. The ITO-$SiO_2$ (polysilazane)-PES substrate thus obtained exhibited 80 $\Omega/\square$ sheet resistance compared to $20 \sim 50\,\Omega/\square$ ITO-glass and visible light transmittance of ITO-$SiO_2$ (polysilazane)-PES film was 83%. The white OLED device fabricated with the ITO-$SiO_2$-PES substrate exhibited 1,100 $cd/m^2$ luminance compared to 11,500 $cd/m^2$ of OLED made with ITO-glass. The power and current efficiencies of the flexible and rigid white OLED were about same level ($1.0 \sim 1.1$ lm/W and $3.1 \sim 3.3$ cd/A, respectively) suggesting that the main reason of the low luminance of the flexible white OLED was high sheet resistance of ITO-$SiO_2$ (polysilazane)-PES substrate.

## REFERENCES

[1] Low, Hong Yee & Chua, Soo Jin. (2002). *Materials Letters*, *53*, 227–232.
[2] Aucha, Mark Dai Joong., Soob, Ong Kian., Ewaldb, Guenther., & Soo-Jina, Chua. (2002). *Thin Solid Films*, *417*, 47–50.
[3] Melpignano, P., Sinesi, S., Rotaris, G., Antonipieri, M., Cicoira, F., Loi, M. A., Muccini, M., Zambonib, R., Gale, M. T., & Westenhöfer, S. (2003). *Synthetic Metals*, *139*, 913–916.
[4] Ryu, G.-S., Choe, K.-B., & Song, C.-K. (2006). *Thin Solid Films*, *514*, 302–305.
[5] Song, C. K., Xu, Y. X., Byun, H. S., Ryu, G. S., Lee, M. W., Kim, K. H., & Lee, C. H. (2004). *Materials Research Society Symposium Proceeding*, vol. 814, p. I8.4.
[6] Lee, Heon, Hong, Sunghoon, Yang, Kiyeon, & Choi, Kyungwoo. (2006). *Microelectronic Engineering*, *83*, 323–327.
[7] Wuu, D. S., Lo, W. C., Chang, L. S., & Horng, R. H. (2004). *Thin Solid Films*, *468*, 105–108.
[8] da Silva Sobrinho, A. S., Latrèche, M., Czeremuszkin, G., Klemberg, J. E., & Wertheimer, M. R. (1998). *J. Vac. Sci. Technol.*, *A 16*, 3190.
[9] Bose, M., Bose, D. N., & Basa, D. K. (2002). *Mater. Lett.*, *52*, 417.
[10] Silva, A. N. R., Morimoto, N. I., & Bonnaud, O. (2000). *Microelectron. Reliab.*, *40*, 621.
[11] Ohishi, T. (2003). *J. Non-Crystatalline solids*, 248–251.
[12] Singh, B., Bouchet, J., Rochat, G., Leterrier, Y., & Fayet, P. (2007). *Surface & Coatings Technology*, 7107–7114.
[13] Henry, B. M., Dinelli, F., Zhao, K.-Y., Grovenor, C. R. M., Kolosov, O. V., Briggs, G. A. D., Roberts, A. P., Kumar, R. S., & Howson, R. P. (1999). *Thin Solid Film*, 500–505.
[14] Grovenor, R. M., Kolosov, O. V., Briggs, G. A. D., Robers, A. P., Kumar, R. S., & Howson, R. P. (1999). *Thin Solid Film*, 500–505.