The low-temperature $a\text{-SiN}_x$ films with high impermeability and high optical gap with application to organic light-emitting diode

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A low-temperature passivation layer ($\leq 100^\circ\text{C}$) with high impermeability and a high optical gap is required in top-emitting organic light-emitting diodes. Hydrogenated amorphous silicon nitride ($a\text{-SiN}_x\text{:H}$) films fabricated by the plasma-enhanced chemical-vapor deposition of $\text{SiH}_4 + \text{NH}_3 + \text{N}_2$ at 100°C fulfill this requirement. Infrared-absorption spectroscopy was used to monitor the permeability of the $a\text{-SiN}_x\text{:H}$ film. The optimum $a\text{-SiN}_x\text{:H}$ film with an optical gap of 3.1 eV was fabricated at a gas ratio of $\text{SiH}_4\text{:NH}_3\text{:N}_2 = 10\text{:}3\text{:}197$ SCCM. The main absorption peaks of the $a\text{-SiN}_x\text{:H}$ films deposited at 70°C did not change at all, even following a 3000-h-long storage test. © 2005 American Institute of Physics. [DOI: 10.1063/1.2089161]

I. INTRODUCTION

Active matrix organic light-emitting diodes,^{1,2} (AMOLEDs) been extensively adopted in flat panel displays. Future development requires panels with denser pixels and a high contrast ratio. The traditional bottom-emitting structure of AMOLEDs (Ref. 2) has a smaller aperture ratio because light is screened by the bottom poly-Si driving circuit. As the pixels shrink further, this problem becomes more serious. The top-emitting structure can be used to increase the aperture ratio^{3,4} of the AMOLEDs.^{5–7} However, the OLED can easily generate dark spots in air because of the permeation of oxygen and water,^{8,9} shortening the lifetime of the OLED and reducing the emission efficiency. Increasing the lifetime of the OLED and the aperture ratio depends on a passivation film on top of the AMOLED to protect the device from oxidation. The film must exhibit high impermeability¹⁰ and a high optical gap such that the emitted light can pass through.

Plasma-enhanced chemical-vapor deposition (PECVD) is used to fabricate highly uniform films of high encapsulating quality and can be used in a low-temperature process. Hydrogenated amorphous silicon nitride ($a\text{-SiN}_x\text{:H}$) films fabricated by PECVD have been extensively applied in passivating semiconductor devices, including silicon solar cells,¹¹ InGaAs/InP heterostructure bipolar transistors (HBTs),¹² and pseudomorphic GaAs high electron mobility transistors (HEMTs),¹³ among others. However, the conventional $a\text{-SiN}_x$ films fabricated by the PECVD of SiH_4 and NH_3 at low temperature ($< 150^\circ\text{C}$) are porous and easily oxidized by H_2O .¹⁴ A film fabricated by the PECVD of SiH_4 and N_2 has a small optical gap which results in the absorption of the emitted light.¹⁵ In this investigation, the $a\text{-SiN}_x$ films deposited by the PECVD of SiH_4 , NH_3 , and N_2 with different ammonia ratios X_g [$X_g = [\text{NH}_3]/([\text{NH}_3] + [\text{N}_2])$] at different temperatures are studied.

II. EXPERIMENT

PECVD is employed to deposit uniform $a\text{-SiN}_x$ films. A series of $a\text{-SiN}_x$ films was fabricated by the PECVD of SiH_4 , NH_3 , and N_2 with different ammonia ratios ($X_g = 0\text{--}0.25$) on a (100) p -type Si substrate. The flow rate of SiH_4 was fixed at 10 SCCM (standard cubic centimeter per minute) and that of $\text{N}_2 + \text{NH}_3$ was fixed at 200 SCCM. The chamber pressure, the rf power density, the deposition time, and the temperature were 0.9 torr, 0.36 W/cm^2 , 30 min, and 100°C , respectively. The thickness and refractive index were measured using an ellipsometer. The $a\text{-SiN}_x$ films were also fabricated on quartz substrates and their optical gaps were measured using a UV-visible spectrophotometer. Finally, $a\text{-SiN}_x$ films with the optimal ammonia ratio were selected at different deposition temperatures ($\leq 100^\circ\text{C}$) and their optical characteristics were examined.

III. RESULTS AND DISCUSSION

Figure 1(a) presents the infrared (IR) absorption spectra of $a\text{-SiN}_x$ films prepared by the PECVD of SiH_4 and NH_3 at 100°C . Their optical gap is 5.3 eV. The figure clearly indicates that the $a\text{-SiN}_x$ film oxidizes after it is exposed to air. The Si–N stretching (900 cm^{-1}), N–H rocking (1170 cm^{-1}), N–H₂ bending (1550 cm^{-1}), and N–H stretching (3350 cm^{-1}) peaks were changed by 1130 min of oxidation to peaks that corresponded to a chemically stabilized Si–O bond, such as in Si–OH stretching (940 cm^{-1}), Si–O–Si stretching (1080 cm^{-1}), and SiO–H stretching ($2800\text{--}3700\text{ cm}^{-1}$). This result reveals that the $a\text{-SiN}_x$ film fabricated at low temperature by the PECVD of SiH_4 and NH_3 has a continuous fractal-like void structure formed from an NH_x cluster,¹⁴ through which oxygen or moisture could pass. Figure 1(b) depicts the IR absorption spectra of $a\text{-SiN}_x$ films that had been prepared by the PECVD of SiH_4 and N_2 at 100°C . No N–H bond absorption was observed, so no N–H bond was present in the film. The figure clearly demonstrates that the $a\text{-SiN}_x$ film does not oxidize in 3000 h, but its optical band gap is only 1.8 eV.

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FIG. 1. The IR spectra of the $a\text{-SiN}_x\text{:H}$ film fabricated by PECVD of (a) SiH_4 and NH_3 and (b) SiH_4 and N_2 at 100°C at different times after removing from the growth chamber.

Figure 2 presents the thickness and optical gap of $a\text{-SiN}_x$ films deposited at different ammonia ratios $X_g = [\text{NH}_3]/([\text{NH}_3] + [\text{N}_2])$. Section II explicates the deposition conditions. The figure indicates that the film thickness de-

FIG. 2. The thickness and optical gaps of $a\text{-SiN}_x$ films deposited at different nitrogen ratios.

FIG. 3. The ESCA spectra of $a\text{-SiN}_x$ film with $X_g =$ (a) 0, (b) 0.015, and (c) 0.025. The composition of silicon and nitrogen in the film are listed in the figures.

creases as the ammonia ratio increases but the optical gap changes abruptly at low X_g . As X_g is varied from 0, 0.015 to 0.025, the optical gap changes from 1.8, 3.2 to 4.0 eV. Electron spectroscopy for chemical analysis (ESCA) was used to elucidate the mechanism of this abrupt change in the optical

FIG. 4. The refractive index of $a\text{-SiN}_x$ films deposited at different nitrogen ratios.

gap. Figures 3(a)–3(c) show the spectra of $a\text{-SiN}_x$ films with $X_g=0$, 0.015, and 0.025. The figures display the silicon and nitrogen content in the film. The figure clearly demonstrates that when there is no ammonia ($X_g=0$), the peak signal consists of two components, associated with Si–Si (99.8 eV) and Si–N (101.6 eV) bonds, revealing that the N concentration is low (25%) but the Si concentration is high. As the X_g increases to 0.015, the Si–Si (99.8 eV) peak decreases; as the N concentration in the film increased from 25% to 32%, the Si–N (101.6 eV) peak increases, indicating that the ammonia molecules were more easily ionized than nitrogen and subsequently combined with Si ions to generate Si–N bonds. At $X_g=0.025$, the Si–Si peak is eliminated and only the Si–N (101.6 eV) peak is present, suggesting that the entire film is transformed into $a\text{-SiN}_x$ film. The increase in the proportion of Si–N bonds increases the optical gap abruptly. However, the proportion of N–H bonds increases with the NH_3 content and the NH_x microvoids tend to join together and yield microchannels, which allow the oxygen or moisture to pass through and oxidize the films. Therefore, the $a\text{-SiN}_x$ film

FIG. 5. The IR spectra of PECVD $a\text{-SiN}_x\text{:H}$ film fabricated at 100, 90, 80, and 70 °C with the NH_3 ratio $X_g=0.025$. The IR spectra of the films were measured at 10 min and 3000 h after the samples were removed from the growth chamber.

FIG. 6. The IR spectra of PECVD $a\text{-SiN}_x\text{:H}$ film fabricated at 100, 90, 80, and 70 °C with the NH_3 ratio $X_g=0.015$. The IR spectra of the films were measured at 10 min and 3000 h after the samples were removed from the growth chamber.

with an ammonia proportion of around 0.015–0.025 can result in high impermeability and a high optical gap. Figure 4 depicts the refractive index of the $a\text{-SiN}_x$ film under different ammonia ratios X_g . It demonstrates that a lower ammonia ratio is responsible for a higher refractive index, a lower optical gap, and a higher Si/N ratio.¹⁶

A series of studies of $a\text{-SiN}_x$ films deposited at 100 °C with different X_g showed that the optimum ratio is either $\text{SiH}_4\text{:NH}_3\text{:N}_2=10\text{:}5\text{:}195$ SCCM ($X_g=0.025$) with an optical gap of 4.0 eV or $\text{SiH}_4\text{:NH}_3\text{:N}_2=10\text{:}3\text{:}197$ SCCM ($X_g=0.015$) with an optical gap of 3.1 eV. Figure 5 presents the IR spectra of the $a\text{-SiN}_x$ film deposited at $X_g=0.025$ at temperatures of 100, 90, 80, and 70 °C, respectively, after exposure to air for 10 min and 3000 h. Only the films deposited at 100, 90, and 80 °C exhibit the same peak magnitude after the 3000 h storage test, but that deposited at 70 °C generated a Si–O–Si peak after the 3000 h storage test. Figure 6 shows the IR spectra of the $a\text{-SiN}_x$ film deposited at $X_g=0.015$ at temperatures of 100, 90, 80, and 70 °C, respectively, after it was exposed to air for 10 min and 3000 h. All peak magnitudes were unchanged after the 3000 h storage test.

FIG. 7. The optical gap of $a\text{-SiN}_x$ films deposited at different temperatures with nitrogen ratio $X_g=0.015$.

FIG. 8. The ESCA spectra of $a\text{-SiN}_x$ films deposited at (a) 100 and (b) 70 °C with the nitrogen ratio $X_g=0.015$.

Figure 7 shows the optical gap of $a\text{-SiN}_x$ films deposited with $\text{SiH}_4:\text{NH}_3:\text{N}_2=10:3:197$ SCCM ($X_g=0.015$) at different temperatures. A lower deposition temperature resulted in a higher optical gap. Figures 8(a) and 8(b) present the ESCA

FIG. 9. The refractive index of $a\text{-SiN}_x$ films deposited at different temperatures with the nitrogen ratio $X_g=0.015$.

FIG. 10. The normalized IR spectra of $a\text{-SiN}_x$ films fabricated with the nitrogen ratio $X_g=0.015$ at 100 and 70 °C.

spectra of films deposited at $X_g=0.015$ at 100 and 70 °C, respectively. As the temperature declines, the Si-Si (99.8 eV) peak decreases relative to the Si-N (101.6 eV) peak and the N concentration rises from 32% to 35%, increasing the optical gap. Figure 9 plots the change in the refractive index with temperature. A lower deposition temperature results in a lower refractive index, a higher optical gap, and a lower Si/N ratio.¹⁶ Figure 10 displays the normalized infrared spectra from Fig. 5 for $a\text{-SiN}_x$ films deposited with $\text{SiH}_4:\text{NH}_3:\text{N}_2=10:3:197$ SCCM ($X_g=0.015$) at temperatures of 70 and 100 °C. The figure clearly reveals that the N-H bonds are larger in films deposited at the lower temperature, 70 °C, indicating that reducing the temperature increases the N content; increasing the proportion of Si-N bonds yields a film with more NH_x voids.

IV. CONCLUSIONS

In summary, the PECVD $a\text{-SiN}_x$ films fabricated with different ammonia ratios X_g were optimized to have a high optical gap and low permeability, to be exploited in top emission AMOLEDs. The IR spectra and the ESCA analysis demonstrate the mechanism of the formation of a high optical gap and low permeability. The optimum ratio at a deposition temperature of 100 °C is $\text{SiH}_4:\text{NH}_3:\text{N}_2=10:3:197$ SCCM ($X_g=0.015$), and the optical gap is 3.1 eV. A temperature of over 70 °C is favorable for depositing the $a\text{-SiN}_x$ film as a passivation layer for top-emitting AMOLEDs. At a lower deposition temperature, more Si-N bonds are formed, increasing the optical gap and generating more NH_x voids, increasing the porosity of the film.

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