Effect of CO₂ Laser on SiNₓ Films Fabricated by Low-Temperature Laser-Assisted Plasma Enhanced Chemical Vapor Deposition

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The fabrication of effective inorganic barrier films using low-temperature processes has become an important issue in the field of flexible electronics. In this study, we investigate the characteristics of SiNₓ films produced by CO₂ laser-assisted plasma-enhanced chemical vapor deposition at low temperature. From measurements of the thickness, surface topography, etch rate, and refractive indices, we demonstrate the enhanced quality of SiNₓ films fabricated by CO₂ laser irradiation. Furthermore, we show that the CO₂ laser irradiation is more effective on small samples, and that its effect also relies on types of substrate because their thermal conductivities affect the spread of heat originating from the CO₂ laser irradiation. From the results presented here, appropriate CO₂ laser configurations, selected according to the type and size of substrate, are shown to enhance the quality of SiNₓ films.

Keywords: Flexible, CO₂ Laser Irradiation, Laser-Assisted Plasma Enhanced Chemical Vapor Deposition (LAPECVD), Organic Light-Emitting Diodes (OLEDs), Barrier Film.

1. INTRODUCTION

Nowadays, inorganic barriers have become more and more important in the field of passivation for electronic devices,¹,² encapsulation for flexible display,³,⁴ Organic light emitting diodes (OLEDs) are the most promising candidate for flexible displays, and they are very vulnerable to moisture and oxygen that degrade the organic devices.⁵ Over the past few years, practical research has focused on thin film encapsulation (TFE) for flexible OLED applications.⁶–⁸ Thin film encapsulation (TFE) is implemented with inorganic and organic multi-layers.³–⁸ The inorganic layer is considered to be a core technology for barrier improvement in combination with, and therefore low-temperature processing of the inorganic layer has become an important issue.⁹,¹⁰ Although glass is used for most display substrates, the recent demand for flexible displays requires novel flexible substrates; therefore, plastic substrates are a current research focus.¹¹,¹² Plastic substrates require low-temperature processing because they have lower phase transition temperatures than glass.¹¹–¹⁴

A number of low-temperature deposition technologies have been introduced to address various problems associated with the flexible devices. The atomic layer deposition (ALD) method was introduced for dielectric and barrier materials because it is a low-temperature process that produces excellent step coverage in a high-density film without pinholes.¹⁵ However, the deposition rate of ALD is too low to be adequately productive for application in the flexible device industry. The plasma-enhanced chemical vapor deposition (PECVD) method can be conducted at a relatively low temperature, and it also offers good step coverage.¹⁶ However, favorable film properties are usually obtained only at processing temperatures above 300 °C. Moreover, damage of the under-layer and substrate originating from excessively energetic ion bombardments have been identified as a huge problem with the PECVD technique.¹⁷

In order to overcome the limitations of the aforementioned methods, several studies have been conducted on depositing thin films at low temperatures using laser-assisted plasma-enhanced chemical vapor deposition (LAPECVD).¹⁸–²¹ In particular, Tsai et al. examined the enhanced formation of a SiNₓ film on a Si substrate using...
CO₂ LAPECVD. However, they used a small Si-wafer substrate of only 1 x 2 cm², and their report did not adequately discuss the thermal effects induced by the CO₂ laser irradiation. In the study presented in this paper, we systematically investigated the formation of the SiNₓ film with CO₂ laser irradiation by varying the type and size of the substrate.

2. EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the LAPECVD system used to deposit the SiNₓ film. The LAPECVD system consisted of a process chamber, a substrate heater, a gas delivery system, a plasma source, a pumping system, a CO₂ laser optical system, etc. A typical capacitively coupled plasma (CCP) source was driven by a single radio-frequency (RF) power supply at 13.56 MHz. The base vacuum pressure was less than 3 x 10⁻⁶ Torr. The different substrates used for the SiNₓ films were a piece of P type (100) Si wafer (20 x 20 mm²), a Si wafer (150 mm in diameter), a piece of glass used as a sample through number 1 to number 5 (20 x 20 mm²), and a glass film (100 x 100 mm²).

During the SiNₓ film deposition, the reactant gases of SiH₄ (1% in Ar balance) and N₂ were supplied, at 1000 and 100 SCCM, respectively, to the process chamber through the mass flow controller (MFC). The process pressure, RF plasma power, substrate temperature and deposition time were 500 mTorr, 50 W, 35 °C and 10 min, respectively. The vertical distance from the shower head to the various substrates was fixed as 35 mm.

A CO₂ laser with a wavelength of 10.6 μm was irradiated into the PECVD system through a ZnSe window. The CO₂ laser’s power was 50 W, and it had a diameter of 6.5 mm. The CO₂ laser beam was irradiated in a direction parallel or inclined (by 1°) relative to the substrate.

The microstructures of the SiNₓ films were observed by field emission scanning electron microscopy (FE-SEM). The Filmetrics F32 and a surface profiler (Alpha-Step IQ, KLA-Tencor) were used to measure the thickness of the SiNₓ films. The refractive index was measured by an ellipsometer (Elli-SE-Uam12, Ellipsco Technology). The roughness of the SiNₓ films was also analyzed by atomic force microscopy (AFM) (NX10, Park Systems). The etch rates were estimated using a mixture of 30 ml of 7:1 buffered oxide etch (BOE) and 120 ml of distilled water.

3. RESULTS AND DISCUSSION

In order to evaluate the effects of the CO₂ laser on SiNₓ deposition, four kinds of deposition methods were used to deposit the SiNₓ films: LAPECVD and PECVD, each in both inclined and parallel deposition conditions. Figure 2(a) presents schematic diagrams of the sample position relative to the CO₂ laser and the substrate for the parallel and inclined conditions. Figure 2(b) shows the different thicknesses obtained by the parallel and inclined deposition conditions at particular points, as determined by Filmetrics. Here, the difference in thickness was obtained by subtracting the thickness of the SiNₓ film deposited by LAPECVD from the thickness deposited by PECVD at the same position. The thickness differences for the middle samples were 90 ± 23 nm. However, the thickness differences for the samples to the left and right were only 11 ± 15 nm and 6 ± 4 nm, respectively. The middle samples showed significant thickness differences because the middle samples were either irradiated by the CO₂ laser or were not irradiated. In the case of the parallel depositions, Sample 1 showed the significant thickness difference because it was the only one irradiated by the CO₂ laser. Samples 2 through 5 were not irradiated by the CO₂ laser and showed no effective thickness difference because these samples were in the shadow by Sample 1.

Figure 3 shows photographs of SiNₓ films on pieces of Si wafers with and without the CO₂ laser irradiation with the thickness of each SiNₓ film denoted in units of nm. All pieces of Si wafer had the same size of 20 x 20 mm² and were deposited for 10 minutes at 35 °C by the PECVD method. The arrow in Figure 3(a) shows the direction of the CO₂ laser irradiation, which had a diameter of 6.5 mm. As shown in the inset of Figure 2(a), all of the pieces of Si wafer in the middle could be irradiated by the CO₂ laser because the holder was inclined by approximately 3.5 mm (1°). Figure 3(b) contains a photograph of SiNₓ films in an inclined holder without the CO₂ laser irradiation. Comparing Figures 3(a and b), it is apparent that only the 5 Si pieces irradiated by the CO₂ laser exhibit a change in color. Therefore, the color differences between the middle samples of Figures 3(a and b) can be attributed to the difference in thickness and refractive index between the samples with and without exposure to CO₂ laser irradiation during the SiNₓ film deposition process.

Pan et al. and Fernandez et al. have reported that SiNₓ and SiOₓ films could be deposited by parallel CO₂ laser irradiation without plasma using SiH₄–NH₃–Ar or SiH₄–N₂O gas mixtures. These researchers suggested that the gas temperature could be high enough to initiate the chemical reaction in the gas phase by the photonic energy of the CO₂ laser. However, as shown in Figure 2(b), the parallel CO₂ laser was not effective in the formation
of SiN<sub>x</sub> film, even though the power density of CO<sub>2</sub> laser was similar to that used by the previous researchers. We believe that this difference can be attributed to the relatively lower deposition rate (under 6 nm/min) by LAPECVD even at higher substrate temperature over 250 °C. In this study, the deposition rate of the SiN<sub>x</sub> film was relatively too high (about 35 nm/min by PECVD) to affect the characteristics of films especially at such a low substrate temperature of 35 °C. Therefore, from our experiments, it could be suggested that the gas decomposition by the CO<sub>2</sub> laser may not have a major effect on the thickness differences of SiN<sub>x</sub> films.

Figure 4 shows the surface and cross-section microstructures of the SiN<sub>x</sub> films deposited by PECVD and LAPECVD for Sample 1 from Figure 3. Comparing Figures 4(a and b), the sample not exposed to CO<sub>2</sub> laser irradiation has many pinholes and a larger grain size than the sample exposed to CO<sub>2</sub> laser irradiation. Figures 4(c and d) show that the sample exposed to CO<sub>2</sub> laser irradiation has a thinner and denser film compared with the unexposed sample, which is similar to their surface microstructures. Moreover, the first sample irradiated by the parallel CO<sub>2</sub> laser (not shown) has a microstructure similar to that of the sample shown in Figures 4(b and d).

Figure 5 shows the surface morphologies of the SiN<sub>x</sub> films deposited by PECVD and LAPECVD in the range of 1 μm × 1 μm. From Figure 5, it is possible to confirm that the sample exposed to CO<sub>2</sub> laser irradiation has a smaller grain size and a denser structure, as in the FE-SEM images. The surface roughness of the SiN<sub>x</sub> films deposited by PECVD and LAPECVD were 3.348 nm and 2.262 nm, respectively. Therefore, it is possible to confirm that the microstructure and the roughness of the SiN<sub>x</sub> films were improved by CO<sub>2</sub> laser irradiation.
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In order to evaluate the film quality, etching tests of the SiNₓ films were performed using a mixture of 30 ml of 7:1 buffered oxide etch (BOE) and 120 ml of distilled water. The sample exposed to CO₂ laser irradiation showed the lower etch rate of 0.13 nm/s compared to the sample not exposed to CO₂ laser irradiation, which had an etch rate of 8.33 nm/s. Etch tests of the SiNₓ films deposited by PECVD at the various temperatures were also performed to compare the effects of CO₂ laser irradiation and substrate temperature. Figure 6 shows the etch rates of the SiNₓ films deposited at various substrate temperatures. Because the density of the SiNₓ films increased when deposited at higher temperatures, the etch rates decreased as the temperature increased. From the results of Figure 6, the effects of the CO₂ laser on the film quality were comparable at the substrate temperature of 250 °C. Moreover, the refractive indices of SiNₓ films with and without exposure to CO₂ laser irradiation were 2.50 and 2.09, respectively. Therefore, the CO₂ laser irradiation improved the quality of the SiNₓ film.

Fig. 4. FE-SEM images of SiNₓ films of Sample 1: (a) surface of microstructure obtained by PECVD, (b) surface of microstructure obtained by LAPECVD, (c) cross-section of microstructure obtained by PECVD, and (d) cross-section of microstructure obtained by LAPECVD.

Fig. 5. AFM images of SiNₓ films for Sample 1: (a) surface morphology obtained by PECVD and (b) surface morphology obtained by LAPECVD.

Fig. 6. Etch rate of SiNₓ films deposited by LAPECVD and by PECVD at various substrate temperatures (inset shows the entire graph).
Figure 7 shows the thickness of SiN$_x$ films deposited by LAPECVD and PECVD on a glass substrate ($100 \times 100$ mm$^2$) and a Si wafer (150 mm in diameter), using the inclined deposition method. In Figures 7(a and b), the CO$_2$ laser irradiated only the middle of the substrates with a spot size of 6.5 mm. In the case of the glass substrate, the color and thickness were changed at only the irradiated region. The thickness differences between the middle 5 positions were $50 \pm 25$ nm, and the thickness differences between the 8 positions on the lines to the right and left were only $4 \pm 3$ nm. However, in the case of the Si wafer, the overall color and thickness were slightly changed by the CO$_2$ laser irradiation, as shown in Figure 7(b). The thickness differences between the middle 5 positions were $20 \pm 6$ nm, and the thickness differences between the 8 positions on the lines to the right and left were $22 \pm 9$ nm. Because all of the process conditions were the same except for the types of substrates, the differences in the thermal conductivity between the glass and Si substrate materials may be one of the major factors determining these results.

To investigate other major factors, the thickness differences between the SiN$_x$ films with and without exposure to the CO$_2$ laser were also investigated using the pieces of Si wafer and glass, as shown in Figure 8. Figure 8 shows that the thickness differences of small pieces of glass and Si wafer were $110 \pm 10$ nm and $90 \pm 23$ nm, respectively. In the case of the Si wafer (150 mm in diameter), the entire region showed similar thickness differences, including the region unexposed to CO$_2$ laser irradiation, whereas in the case of the Si pieces, only the region exposed to CO$_2$ laser irradiation showed the significant changes in thickness. In the case of glass, only the region exposed to CO$_2$ laser irradiation showed the significant changes in thickness. Moreover, the thickness differences of the smaller samples were larger than those of the larger samples, regardless of the types of substrates, and the thickness differences of the glass substrates were larger than those of the Si substrates.
of the Si wafers for similarly sized samples. The Si wafer could easily spread the heat originating from the CO₂ laser irradiation to peripheral regions owing to its high thermal conductivity of 148 W/mK. However, the glass’s thermal conductivity is 100 times lower, at 1.1 W/mK (Corning EAGLE XG), than that of Si, and therefore the glass does not easily spread the heat to the peripheral regions. From these results, it could be suggested that the temperature change originating from the CO₂ laser irradiation of the substrates may be the major factor for improving the characteristics of SiNₓ films such as thickness, refractive index, etch rate, microstructure, morphology, etc.

### 4. CONCLUSION

In this study, the effects of CO₂ laser irradiation on the characteristics of SiNₓ films were investigated. SiNₓ films irradiated by CO₂ lasers showed reduced thicknesses, denser microstructures, lower etch rates, and higher refractive indices, owing to the additional energy offered by laser irradiation. From the investigations of parallel and inclined deposition methods, only the directly irradiated samples exhibited changes in the characteristics of the SiNₓ films, implying that direct illumination is much more efficient in adding extra energy by laser. Moreover, the thickness differences of the larger samples were larger than those of the larger samples, regardless of the type of substrate, and the thickness differences of the glass substrates were larger than those of the Si wafers for similarly sized samples. Therefore, it could be suggested that the heat from CO₂ laser irradiation improves the quality of SiNₓ films, and LAPECVD could be used for low-temperature processing of water vapor barrier layers and dielectric layers, using an adequate CO₂ laser.

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### References and Notes


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