Efficient Methodology for Increasing Atomic Layer Deposition Throughput by Optimizing Deposition Rate of SiO2 Film

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Abstract

Low deposition rate limited the mass production of atomic layer deposition in display manufacturing. In this work, a 29% enhancement in the deposition rate was achieved through the optimization of process parameters and the selection of precursors, thereby fulfilling the requirement of the tact time in production fabrication. The application of ALD was expanded through the study of the growth mechanism of SiO_2 films.

Author Keywords

OLED; PEALD; Deposition rate; Precursor; Thin film encapsulaiton (TFE);

1. Introduction

With the advancement of manufacturing technology for organic light-emitting diodes (OLEDs), OLEDs have found extensive applications in mobile terminals such as smartphones and tablets. The organic light-emitting materials and cathode are sensitive to atmospheric moisture and oxygen. Therefore, an encapsulation structure is required to provide sufficient water vapor barrier properties. The improvement of the reliability performance of OLEDs affects the expansion of application scenarios, such as vehicles or outdoor environments.

Atomic Layer Deposition (ALD) is frequently cited as a method for improving OLED longevity and reliability. ALD is a thin film deposition technique that relies on the sequential application of gas-phase chemical processes. These precursors interact with the surface in a self-limiting, sequential manner, resulting in thin film deposition through repeated exposure.

One of the factors limiting the large-scale application of ALD technology in OLED manufacturing is its low deposition rate. The choice of precursor is crucial for ALD processes at a low temperature (< 100 ℃). It significantly influences the processing time and the various properties of the deposited film, including step coverage, uniformity, water vapor transmission rate (WVTR), density, and other characteristics. The existence of additional reaction sites, such as amine groups and the number of Si atoms in a molecule, affects the growth rate.

This paper introduces research on increasing the deposition rate of Silicon dioxide (SiO2) thin films prepared by plasma-enhanced atomic layer deposition (PEALD) at a low temperature. The deposition rate can be improved through the optimization of process parameters and the selection of multi-substituent precursors. Growth per Cycle (GPC) and refractive index (R.I.) were the major parameters for studying deposition rate increase. The GPC was significantly improved from 1.26 Å/cycle to 1.63 Å/cycle. Water vapor resistance of SiO2 films was also improved by increasing the plasma time. Excellent step coverage and compactness contributed to the improvement of the reliability of OLED devices. No pixel shrinkage or dark spots appeared after storing in an environment of 85% humidity and at 85 ℃ over 1000 hours.

2. Method

2.1 Fabrication of the Silicon Oxide thin films by PEALD

The SiOx thin film was fabricated by PEALD at low-temperature conditions under 100℃. Purge and carrier gas were continuously applied during the process. The effect of process parameters on the growth rate was studied, such as plasma time or power and so on. Three different precursors were used in order to achieve the increase of the deposition rate of ALD SiOx film.

2.2 Evaluation of the properties of the thin film

The growth of the thin films and refraction index were detected by Ellipsometer (J.A.Woollam, M-2000X). In general, the refractive index (R.I.) of the film is positively correlated with its density. R.I. is often used to indirectly characterize film density. Mocon II was used to detect the barrier properties before and after the introduction of the modified layers.

2.3 Evaluation of the OLED Device

The encapsulation effect was illustrated by a reliability test at accelerated climate conditions of 85℃/85% relative humidity. Whether there was pixel shrinkage was observed in certain intervals. Lifetime test was measured by IVL equipment.

3. Results

3.1 The increase of the GPC

Growth rate per cycle (GPC) is determined by characteristics of precursors and film materials, and by deposition temperature. Thickness is determined by the number of cycles. Thickness is determined by the number of cycles.

3.1.1 The influence of the process parameters

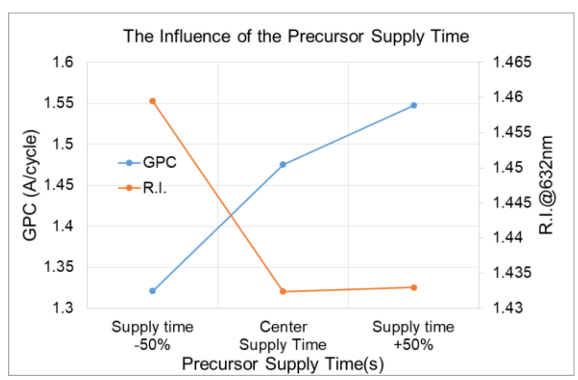

Figure 1. The influence of the supply time

The supply time of the precursor determines the extent of adsorption on the surface. As the supply time for precursor adsorption increases, surface adsorption and growth per cycle

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(GPC) increase. GPC increased from 1.32A/cycle to 1.55A/cycle. As illustrated in the figure 1, an increase in precursor supply time led to an increased reaction rate, resulting in a decrease in the refractive index. The refractive index decreased from 1.46 to 1.432 when the plasma process duration fixed, indicating a decrease in film density.

The duration of plasma exposure is inversely proportional to the GPC of the ALD film. The plasma processing time directly influences both the degree of oxidizer dissociation and the quantity of plasma generated. A higher level of dissociated oxidizing plasma facilitates a more complete oxidation reaction, resulting in a slower film formation rate. Consequently, this reaction tends to be ALD-like.

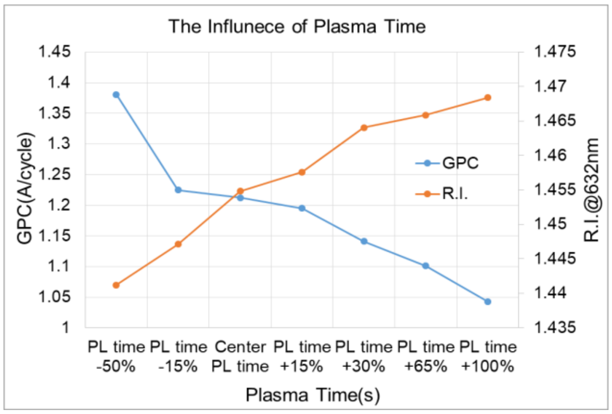


Figure 2. The influence of the plasma time

As shown in Figure 2, R.I. increases as GPC decreases. Generally, R.I. Of the film exhibits a positive correlation with its density. This observation aligns with the established theory that slower deposition rates yield denser films.

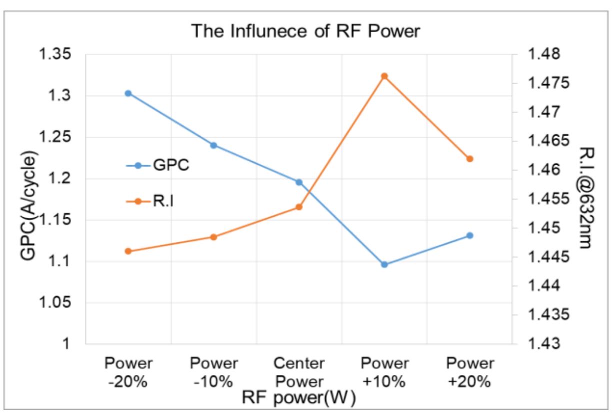


Figure 3. The influence of the RF Power

The effect of RF power is similar to that of plasma process time. An increase in RF power leads to greater dissociation of oxidizer plasma and a more sufficient oxidation reaction. The increase of power enhances film density and uniformity, reduces pinholes and defects, and improves overall film quality.

When RF power increased, GPC initially decreased and subsequently increased, reaching a minimum value of 1.096A/s when power increased by 20%. Concurrently, the refractive index exhibited an inverse trend, increasing and then decreasing to reach a maximum value of 1.476.

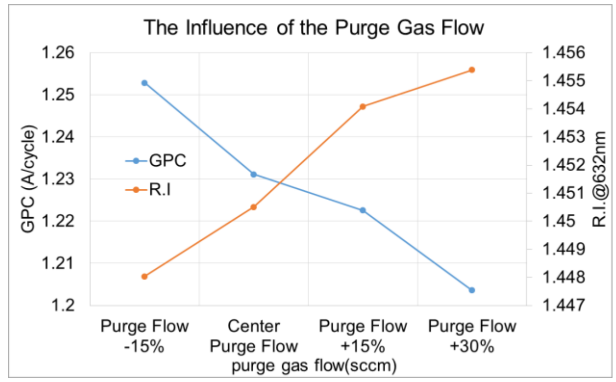


Figure 4. The influence of the purge gas flow

The purge gas is continuously applied during the process to remove non-surface-adsorbed precursors and eliminate unreacted oxygen plasma. This ensures that the deposited thin film results from ALD-like rather than CVD-like processes. An increase in purge flow leads to a decrease in GPC, as by-products are effectively removed, resulting in denser film growth. Furthermore, enhancing the flow of purge gas facilitates the removal of O- species that have been plasmonized but have not participated in oxidation reactions.

This approach serves two purposes: firstly, it helps prevent residual oxygen plasma from damaging OLED devices; secondly, it mitigates the risk of re-collision between O- species, which could lead to the formation of O2 and O3. Figure xx illustrates the trend of GPC as purge gas flow increases. Specifically, GPC rises while the refractive index decreases with increasing purge gas flow.

3.1.2 The influence of the Precursors

The number of amine groups and silicon atoms in the precursor's molecule played significant roles. These factors influenced the adsorption behavior of the precursor on the surface, subsequently affecting the deposition rate and quality of the thin films.

The variation in the number of amino groups resulted in differing decomposition reaction processes of precursor molecules on the surface. This variability influenced whether these precursor molecules could be fully decomposed on the surface, ultimately leading to differences in both the ALD reaction mechanism and the film growth process. The charge effect and volume effect of amino groups also affected their reactivity.

In comparison to the mono-substituted precursor used as a reference, the precursor containing two amine groups (precursor A) facilitated a greater distribution of positive charge on the silicon atom, potentially enhancing the reaction activity of the precursor during the initial stage of decomposition. Precursor A exhibited faster GPC and possessed a higher refractive index. Overall, increasing the number of amine groups resulted in the precursor having relatively lower reaction activation energy during the entire ALD reaction process, making it most suitable for low-temperature deposition processes.

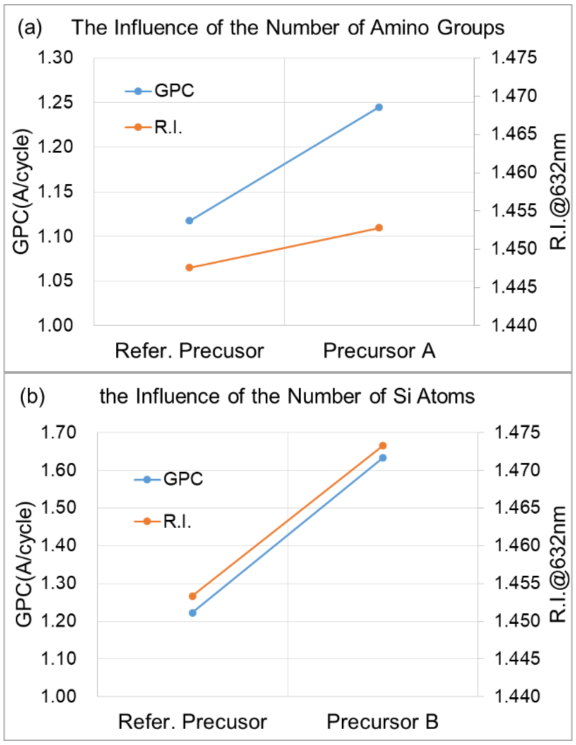


Figure 5. The influence of the Precursor A (a) and Precursor B (b)

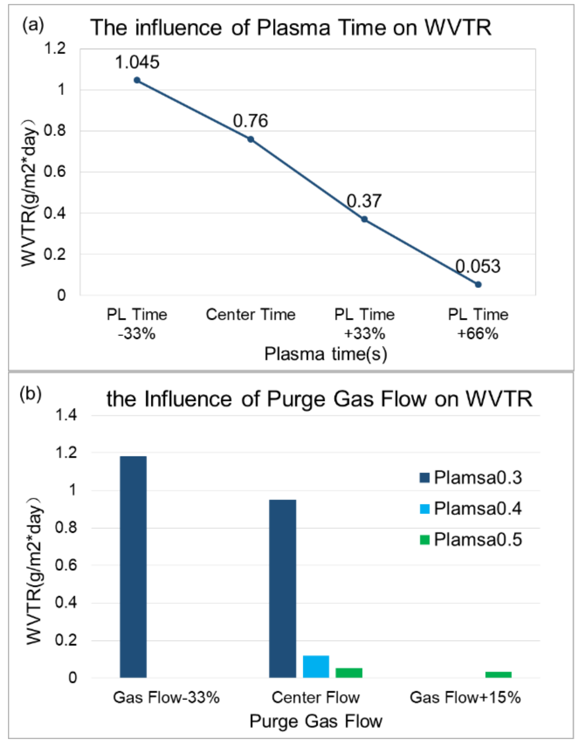


Figure 7. The influence of the plasma time and purge gas flow on WVTR

Precursor molecules containing more than one silicon atom could form a greater number of molecular fragments capable of participating in the reaction after adsorption and dissociation, thus enabling faster formation of the silicon oxide thin film. Compared with the reference precursor, the GPC of precursor B increased by 130%~160%, as shown in the figure 5(b) &6. The presence of more dissociated fragments also allowed for adjustment of the oxidation degree over a wider range, resulting in larger upper and lower limits of the refractive index compared to those of the reference precursor.

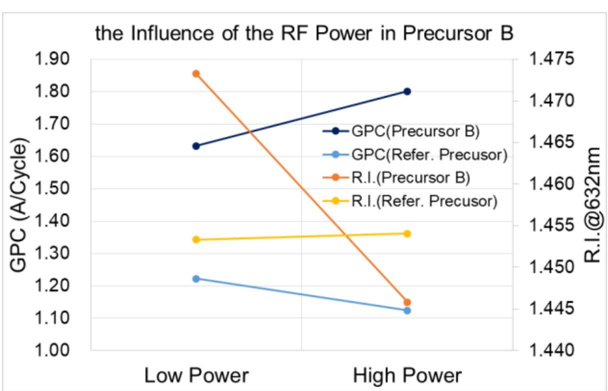


Figure 6. The influence of the Precursors B

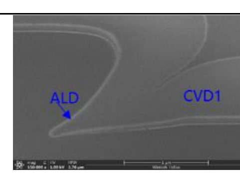
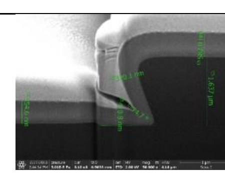
3.2 The properties of the ALD SiOx thin film

When the source supply time was fixed, extending the plasma activation time enhanced the film density and reduced the water vapor transmission rate (WVTR) test results.

$$\Delta WVTR = \frac{WVTR_{After\ RA} - WVTR_{Before\ RA}}{WVTR_{Before\ RA}} \times 100\%$$

While increasing plasma activation time effectively reduces WVTR, excessive plasma activation time may result in damage to OLED devices. Therefore, to further reduce the WVTR, it is necessary to increase the gas flow of the purge gas to effectively remove non-reactive species such as O2+, O+, O2-, and other ions, thus reducing the damage caused by ionic bombardment to sensitive OLED materials.

Table.1 The comparison of step coverage between ALD and CVD

Item	ALD	CVD
Side coverage	97%	64%
Bottom coverage	100%	72%
SEM		
ΔWVTR	2.61%	10528%

The self-limited surface reactions ensure that the films deposited by ALD grow in an atomic layer-by-layer manner, which facilitates precise control of thickness and conformal deposition of thin films, even on high-aspect-ratio nanostructures.ALD has demonstrated superior step coverage (S.C.) performance. When deposited in an inverted trapezoidal photo spacer, the S.C. of the ALD film exhibited nearly 100% conformality, whereas that of the CVD film ranged from 60% to 70%.

3.3 The Reliability and lifetime performance of OLED device

For vehicle or outdoor OLED products, the reliability specification was established at over 500 hours during the steady-state temperature and humidity bias life test (commonly referred to as the 85℃/85% test).

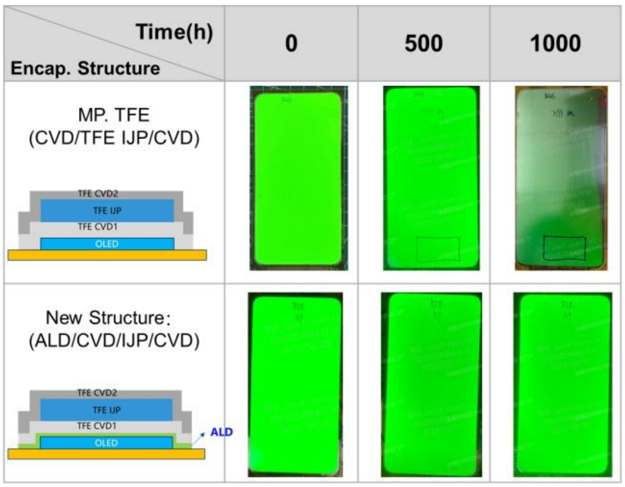


Figure 8. The influence of the Precursors B

The barrier properties of the new developed TFE structure with the introduction of ALD SiOx exhibited significant enhancement. Figure 8 summarizes the results of the reliability tests in this study. After being stored in an environment with 85% humidity at a temperature of 85 ℃ for over 1000 hours, no pixel shrinkage nor dark spots were observed in the new structure in this study, while there was obvious side failure in the reference samples. In the lifetime test, compared to the reference structure, the lifetime of the new structure was increased by 63%, 52%, and 48% at T90, T85, and T80, respectively.

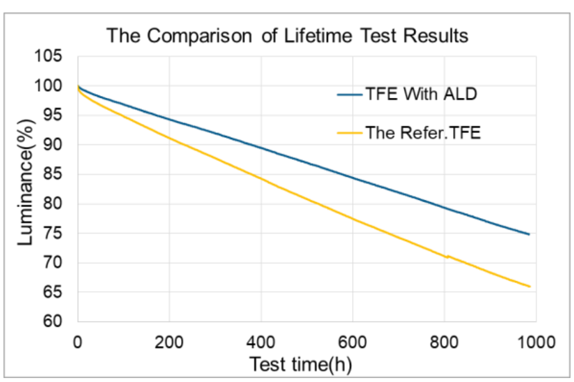


Figure 9. The IVL results of lifetime

The excellent step coverage and compactness of the ALD thin film contribute to the reliability performance of the new structure. It could effectively cover the micro size particles, reduce the point discharge, and consequently improve the stability of the OLED device. Additionally, the tiny pinholes on the electrode surface of the OLED device were filled with ALD, thus improving the device lifetime.

4. Discussion

In this study, a 29% increase in the deposition rate of Silicon dioxide (SiO_2) film was achieved. It was fabricated by prepared by PEALD at low temperature. The deposition rate can be enhanced by optimizing the process parameters and choosing a multi-substituent precursor. The growth per cycle (GPC) can be remarkably increased from 1.26 Å/cycle to 1.63 Å/cycle, thereby fulfilling the requirement of the tact time in production fabrication. The WVTR of the SiO_2 films could be decreased by extending the plasma time and increasing the flow of the purge gas. No pixel shrinkage or dark spots were observed after storage in an environment with 85% humidity and at 85 ℃ for over 1000 h. A 48% increase was noted in the T80 lifetime test. The application scope of ALD technology can be broadened by investigating the growth mechanism of SiO_2 films prepared by ALD.

5. References

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