

Influence of Thin Fluorine Resin Film on DUV LED Packaging Devices

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Abstract: Amorphous fluorine resin is a promising material that can be used for the encapsulation of deep-ultraviolet light-emitting diodes (DUV LEDs) to promote the light output, due to its light characteristics which mean it shows no absorption in the DUV wavelength region. However, obvious decay and high cost are the problems faced by fluorine resin. In this study, thin-fluorine-resin-film-packaged DUV LEDs were fabricated by the drip-coating method and the characteristics were tested. The results show that the light output power increased from 4.95 mW to 5.44 mW at 40 mA, and the cost of fluorine resin can be reduced to ~10%. In addition, no degradation during the aging was observed. However, when the light output power reached 12 mW or higher, >10% decay was observed after aging for 1000 h. In conclusion, thin-fluorine-resin-film-packaged DUV LEDs can achieve 10% light output power enhancement by using less fluorine resin material, and the material is more applicable to low-power DUV LEDs.

Keywords: deep-ultraviolet light-emitting diode; fluorine resin; light output power; reliability



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1. Introduction

Over the last three years, the demand for deep-ultraviolet (DUV) light sources with wavelengths between 250 nm and 300 nm increased rapidly due to the spread of the COVID-19 pandemic. Due to their advantages of being mercury-free, having long lifetimes, being small in size and being easily integrated, nitride-based DUV light-emitting diodes (LEDs) have been attracting attention, which are considered to be an alternative to mercury lamps [1–3]. However, compared with blue LEDs, the external quantum efficiency (EQE) of DUV LEDs remains low and degrades significantly with a decreasing wavelength due to immature epitaxial growth and process technology [4]. For blue LEDs (around 455 nm), an EQE of over 80% has been achieved [5]. For DUV LEDs (wavelengths between 250 nm and 300 nm), EQE values are below 10% [6]. As an important factor of EQE, the light-extraction efficiency (LEE) is as low as 9% without any assisted light extraction [7,8]. The main reason for low LEE is the refractive index contrast between the chip and the environment [9,10]. Light propagating outside the escaping cone will be reflected back to the chip and absorbed by active layers, p-type layers and electrodes that have low reflectivity in the DUV region. Many works have been carried out to increase the LEE: for example, pattern sapphire substrates were used, n- and p-reflective electrodes were proposed and new materials and designs were used for encapsulation [11,12].

Resin materials are commonly used in blue LED packaging, since their refractive index is located between the chip and the air, which can increase the critical angle of an escaping cone and promote the light propagating out of the chip to increase the LEE.

Si-O-based polymers exhibit absorption when the wavelength is below 300 nm, causing the materials to have low transmittance in the ultraviolet region, and so cannot be used in DUV LED packaging devices. Amorphous fluorine resins, which have almost no absorption in the DUV region, can be used for the encapsulation of DUV LEDs as promising new materials [13,14]. In previous studies, Yamada et al. discovered that polymerized perfluoro-4-vinyl-1-butene (BVE), having a five-membered ring with a single oxygen, was suitable from the industrial viewpoint [14], and amorphous fluorine resin with the end functional group of $-CF_3$ achieved high UV transparency and excellent UV durability [13]. Nagai et al. found that a 50% light output power enhancement could be achieved by forming a hemispherical encapsulation layer [15]. Peng et al. also found that a 16.5% light output power enhancement could be achieved by doping AlN nanoparticles into fluorine resin [16]. However, in all studies, at least 10% decay was observed after aging when the fluorine resin was used. On the other hand, the cost of fluorine resin is very expensive, and therefore we want to determine the applicable scope of fluorine resin and a method of increasing the light output power by using fewer materials.

In this study, we fabricated DUV LEDs packaged with thin amorphous fluorine resin film by using the drip-coating method. Different thicknesses of fluorine resin coating and different output powers of DUV LED packaging devices were prepared. The influence of characteristics and reliability were studied. The results reveal that when using thin amorphous fluorine resin film for DUV LEDs' packaging, a ~10% increase in the light output power was achieved, and no influence during the aging time was found in the low-power device.

2. Materials and Methods

A $3.5\text{ mm} \times 3.5\text{ mm} \times 0.5\text{ mm}$ AlN ceramic submount (Hunan Tongdaxin Electronic Technology Co., Ltd.) with a Au layer on the surface was used to fabricate the DUV LED packaging device. Flip-chip LEDs (Photon Wave Co., Ltd., South Korea) with AuSn layer on the electrodes were used as the DUV light sources. The average wavelength was 274.1 nm and the average voltage was 5.8 V. Three commercial types of chips were chosen, and the sizes were $0.25\text{ mm} \times 0.5\text{ mm}$ (Chip A), $0.5\text{ mm} \times 0.5\text{ mm}$ (Chip B) and $1\text{ mm} \times 1\text{ mm}$ (Chip C). A zener diode (chip integration) with a size of $0.16\text{ mm} \times 0.4\text{ mm}$ was used as a protective element. Amorphous fluorine resin with trifluoromethyl ($-CF_3$) ends (Ningbo Jiaima Material Technology Co., Ltd., Ningbo, China) was used and dissolved in electronic fluoride solution (FC-40, 3M); the concentration of the fluorine resin was 8%. The manufacturing process is shown in Figure 1. Chip and zener diode were placed on the submount by using no-clean flux (WHP-002, Shenzhen Aoniu Technology Co., Ltd., Shenzhen, China), and then bonded to the submount with the eutectic temperature at $320\text{ }^\circ\text{C}$ for 1 min. The drip coating was implemented as follows: amorphous fluorine resin solution was dripped once on the surface center of the chip by pipette, with one drop being approximately $4\text{ }\mu\text{L}$. Then, the resin was cured by stewing at room temperature for 2 h and then for 24 h. Different thicknesses of fluorine resin film were obtained by repeating the dripping and curing process for different numbers of times.

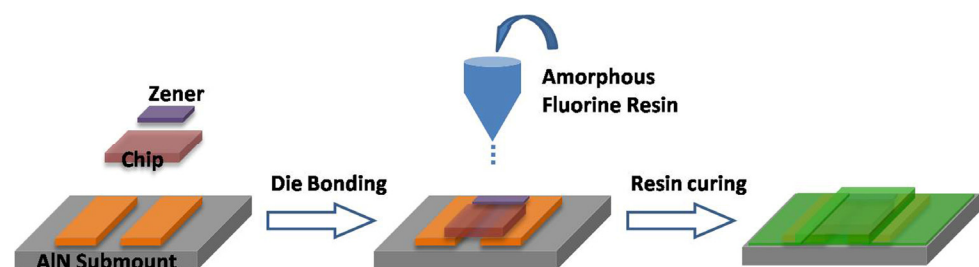


Figure 1. Manufacturing process of DUV LED packaging device.

The absorption spectra of amorphous fluorine resin film were characterized by using an ultraviolet spectrophotometer (Techcomp UV2600). The morphologies of the resin

cross-section were observed by using a field-emission scanning electron microscope (SEM, Hitachi SU3500). The photoelectric characteristics were measured by using a calibrated integrating sphere (Everfine ATA-500UV) under DC current condition. The reliability of the packaging devices was tested by using a high-power aging tester (JXS-12-500). All measurements were performed at room temperature.

3. Results and Discussion

Figure 2 shows the structure and the absorption spectra of amorphous fluorine resin. The fluorine resin has a trifluoromethyl ($-\text{CF}_3$) end, which has been shown to have a more stable performance in DUV devices [13]. To measure the absorption spectrum of amorphous fluorine resin, the fluorine resin film was fabricated on a $45 \text{ mm} \times 20 \text{ mm}$ quartz glass, and the thickness of the film was approximately $40 \mu\text{m}$. The absorption spectrum of the sample was compared with the quartz glass which had no fluorine resin film on it. As shown in Figure 2, the absorption spectra of the quartz glass with fluorine resin film were almost unchanged when the wavelength was between 200 nm and 500 nm, indicating that the fluorine resin has almost no absorption in this wavelength range.

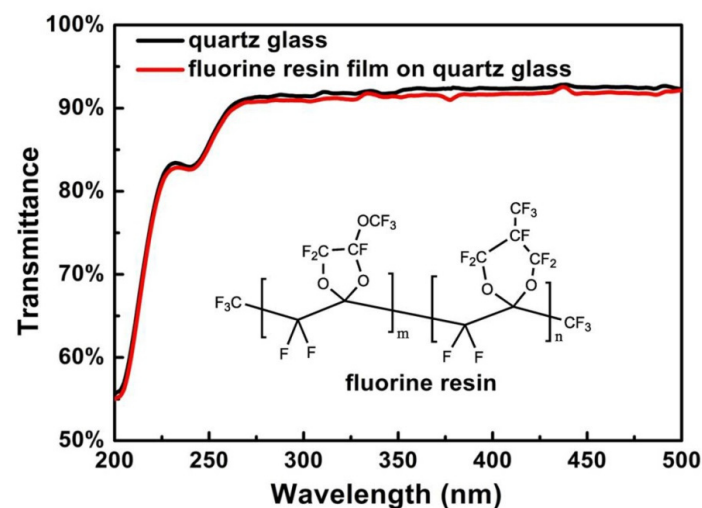


Figure 2. Absorption spectra of amorphous fluorine resin between 200 nm and 500 nm. The resin's structure is shown inside.

Chip A was used first for the study of the fluorine-resin-packaged device. The top view of the packaging device is shown in Figure 3a,b. When the fluorine resin solution was dripped on the device, hemispherical resin covered the surface of the chip and part of the submount. After curing, the fluorine resin formed a transparent thin film on the surface of the device, and both the chip and zener diode were coated by the fluorine resin film. Since the T_g of the fluorine resin in this study was 170°C , the thermal stability of fluorine resin was tested by setting up an experimental point at intervals of 10°C from 170°C to 210°C and then to 240°C . No bubble was observed in the sample when the temperature was below 210°C , which is shown in Figure 3c–g. However, as shown in Figure 3h, when the temperature came to 240°C , the bubbles that existed between the film and submount could be observed. This indicated that the highest tolerance temperature of the fluorine-resin-packaged device was about 210°C .

In Figure 4, we present the cross-sectional SEM image of fluorine-resin-packaged devices that had been cured for 24 h with different dripping times. As shown in the image, fluorine resin covered both the top and side surfaces of the chip, forming a thin film overcoating the outside. We used the thickness of the film in the middle of the top surface to characterize the fluorine resin film, which is marked with d in Figure 4a. As shown in Figure 4e, the film thickness is only tens of micrometers, and with the increase in times the dripping was applied, the thickness of the film increased nearly linearly, from $36.33 \mu\text{m}$ to $74.58 \mu\text{m}$. In addition, as can be seen in Figure 4a–d, the fluorine resin film was too thin

to cover the chip completely when dripping only once, and the top edge of the chip was almost exposed to the air. When the dripping was performed more than two times, the chip was covered by fluorine resin completely and no obvious area could be found to be exposed outside. On the other hand, a crack between the film and the chip could be found at the bottom of the chip's side surface in all samples, as shown by the arrow. This may be due to the internal stress forming in the film and the poor adhesion of the fluorine resin material. With the increasing number of drip coating applications, the internal stress in the film also became larger, which resulted in the crack extending upward along the side surface. In the crack region, the surface of the chip was still in contact with the air; this may have affected the result of promoting light out of the chip.

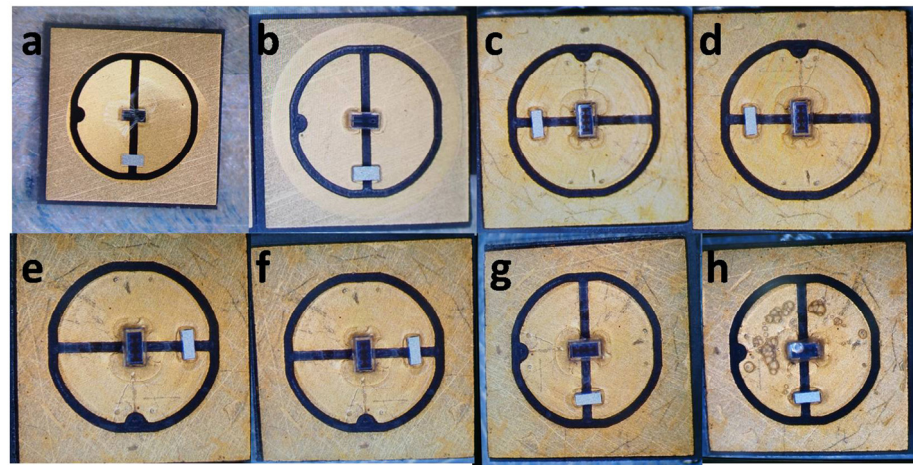


Figure 3. Top view of fluorine-resin-packaged device (a) before curing and (b) after curing. Device after heating to (c) 170 °C, (d) 180 °C, (e) 190 °C, (f) 200 °C, (g) 210 °C and (h) 240 °C for 3 min.

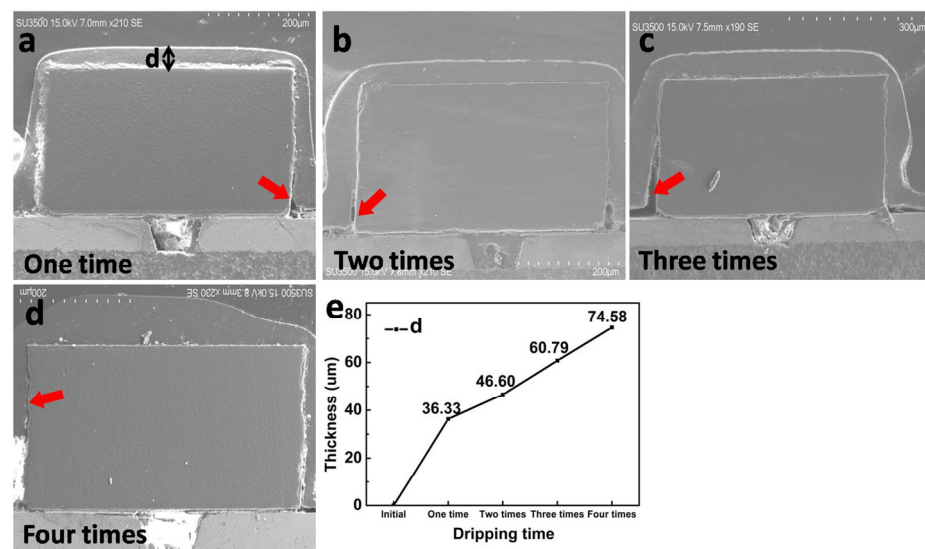


Figure 4. (a–d) Cross-sectional SEM image of fluorine-resin-packaged devices with different numbers of drip coatings, crack is shown by the red arrows. (e) Thickness of the fluorine resin.

Figure 5 shows the characteristics of DUV LED packaging devices with different thicknesses of fluorine resin film at 40 mA. At the same time, the result of devices without fluorine resin is also shown in the figure, which we called the initial value. As shown in Figure 5a, when the curing time was 2 h, the light output power improved gradually from 4.95 mW to 5.86 mW with the increasing dripping applications, which had a rise of 18.41%. After curing for 24 h, the trend of the curve changed. The light output power improved from 4.95 mW to 5.44 mW when dripping two times, which had a rise of 9.87%;

however, when the dripping was performed more than two times, the light output power was reduced to ~5 mW, which was almost unchanged compared with the initial value. Compared with the result of cross-sectional SEM, the reason may be that when the number of drip coatings was lower, the fluorine resin film was too thin to cover the whole surface of the chip. With the increase in drip coatings, the thickness of the film also increased, which formed an overall coverage of the chip and promoted more light to be emitted. However, due to the presence of the crack appearing during the curing process, as shown in the cross-sectional SEM image, the surface of the chip in the crack region was still in contact with the air, and as DUV light needs to pass through the air in the crack and then through the reflection and absorption of the fluororesin layer to emit out, the light output power of the packaging device after complete curing reduced compared with the device when curing for just 2 h was not sufficient. When the drip coating was applied more than two times, the crack became too large, and light output power had no clear increase after complete curing, although it increased obviously after 2 h of curing. The result also revealed that if the crack can be controlled, a larger enhancement of light output power can be received. Table 1 shows the result of light output power enhancement and cost, which are compared with a previous study. Although the enhancement in this work is still lower than 50% [15], the cost is only ~10%. This may be more suitable for industrial production applications.

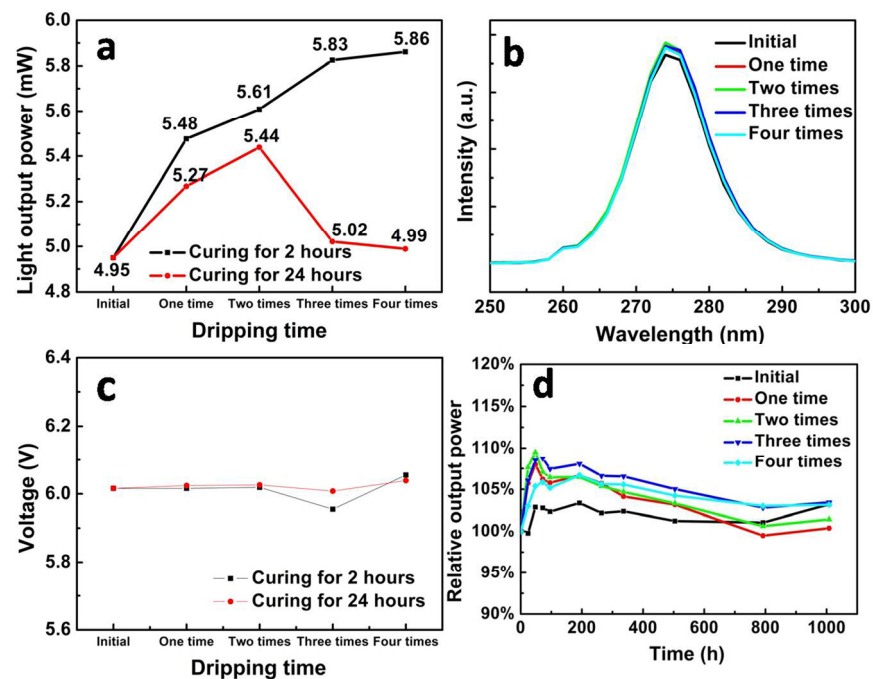


Figure 5. (a) Light output power of fluorine-resin-packaged device, (b) electroluminescence (EL) spectra of fluorine-resin-packaged device after curing for 24 h, (c) voltage of fluorine-resin-packaged device and (d) light output power decay for fluorine-resin-packaged device after curing for 24 h. All measurements were performed at 40 mA.

Table 1. Light output power enhancement and cost of fluorine resin in different studies.

	Packaging Form	Enhancement of Light Output Power	Consumption of Fluorine Resin (g/pcs)	Cost of Fluorine Resin (USD/pcs)
This study	Thin film	~10%	0.00064	0.0277
Previous study	Hemisphere	~50%	0.00470	0.2036

Figure 5b shows the electroluminescence (EL) spectra of the fluorine-resin-packaged device. The peak wavelength was ~275 nm, and there was no obvious shift in wavelength

in the EL spectra after fluorine resin was used for packaging. Figure 5c shows the voltage of the fluorine-resin-packaged device, the voltage was around 6 V, and no significant change was observed. The results indicated that fluorine resin only affected the light output power of the device, and there was no effect on the wavelength and the voltage. Preliminary reliability tests on fluorine-resin-packaged devices are shown in Figure 5d. After aging for 1000 h, the devices were stable under a direct current (DC) mode operation current of 40 mA, and no degradation was observed. The light output power remained over 100% for all devices, better than the at least 10% decay in previous studies [15,16], indicating that fluorine resin has no influence on the lifetime characteristic under this level of light output power.

In order to verify whether the thin fluorine resin film can also be beneficial in the higher light output power of DUV LED packaging devices, Chip B and Chip C were used in the samples by dripping fluorine resin two times and the curing time was 24 h. The test current was 100 mA for Chip B and 350 mA for Chip C, respectively. The photoelectric and reliability characteristics are shown in Figure 6. As can be seen in Figure 6a, the light output power improved from 12.78 mW to 13.96 mW at 100 mA with a rise of 9.23% for Chip B, and the light output power improved from 49.82 mW to 55.01 mW at 350 mA with a rise of 10.41% for Chip C. The results prove that a ~10% enhancement of light output power can be achieved when fluorine resin is used for packaging. However, as the preliminary reliability test result shows in Figure 6b, after aging for 1000 h, the relative output power of the fluorine-resin-packaged device with Chip B decayed by 11.26% at 100 mA, while no decay was observed in the devices without fluorine resin at the same current. At the same time, the reduction was 16.99% for Chip C with fluorine resin compared with bare Chip C at 350 mA. This result may have been caused by DUV-induced photolysis related to the two oxygen atoms in the five-membered ring [14]. When the light output power is 12 mW or larger, obvious decay is observed, the fluorine resin material is still unstable for high-power DUV applications.

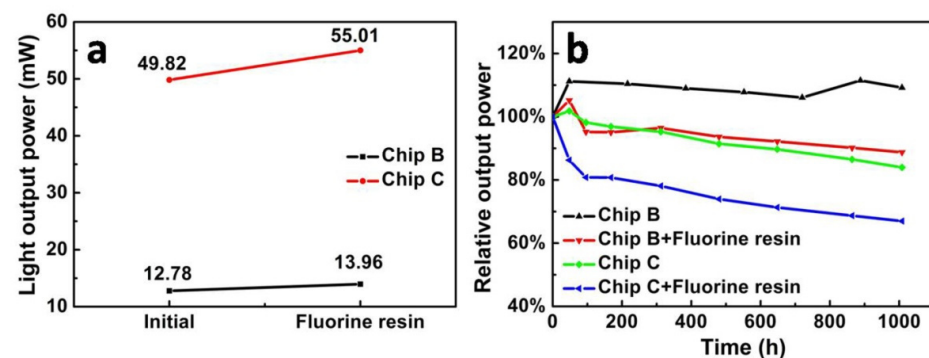


Figure 6. (a) Light output power of devices with Chip B and Chip C, (b) light output power decay for devices with Chip B and Chip C.

4. Conclusions

We have fabricated a thin amorphous fluorine-resin-film-packaged DUV LED device by using the drip-coating method. Tens of micrometers of thin fluorine resin film were formed by using a small amount of fluorine resin solution. Due to the existence of cracks, the enhancement of light output power cannot be increased continually with an increasing thickness of the fluorine resin film. In this condition, the maximum enhancement of light output power was ~10%. At the same time, the consumption of the fluorine resin solution was only 8 μ L, which means the cost of fluorine resin can be reduced to ~10%. In addition, no effect on the wavelength and the voltage was observed, and no degradation was observed after aging for 1000 h on Chip A, for which the light output power was about 5 mW. However, when the light output power reached 12 mW or higher, as in Chip B and Chip C, at least 10% decay was observed after aging for 1000 h. Under these circumstances, the fluorine resin material is more applicable in low-power packaging.

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