# Improved performance by plasma-treated silicate phosphor particles with a sol–gel derived protective coating of indium oxide

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## ABSTRACT

The optical properties and reliability of silicate phosphor was fairly improved by an amorphous $In_2O_3$ protective coating on plasma-treated phosphor particles. The $In_2O_3$ layers were coated using a conventional sol–gel method with alkoxide precursor in $N_2$ gas. The surface morphology of silicate particles was smoother after Ar-plasma surface modification. When plasma surface treatment of the phosphor was applied before sol–gel coating, the $In_2O_3$ coating was almost 3-times thicker, and the surface of the phosphor particles was smoother, than could be obtained when sol–gel coating was not preceded by plasma treatment. This was because the treatment caused the surface to become hydrophilic. The light absorption rate and quantum efficiency were increased from 75.3% and 93.8%, to 79.2% and 95.7%, after plasma-treated $In_2O_3$ coating. Bare silicate phosphor used in 450-nm vertical-type LEDs, displayed 10% decreased optical output, whereas $In_2O_3$-coated phosphor showed just 3% decreased optical output after 1000 h of input current at 350 mA; under conditions of high humidity and high temperature.

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## 1. Introduction

Light-emitting diodes (LEDs) have already started to replace earlier sources of illumination (incandescent bulbs, fluorescent lamp) due to their high luminous efficiency and high reliability [1–3]. To produce white light in conventional GaN LEDs, various phosphor materials have been utilized in which a blue (450 nm) LED pumps a phosphor to generate a corresponding light with longer wavelength, through an energy down-conversion [1,4]. Recently, as the demand has increased for enhanced-performance LED lighting (e.g., higher color rendering index (CRI) and longer lifetimes), the need for phosphors with wider coverage of emission spectra and higher reliability has also increased [1,3,5]. Although there have been many reports of novel phosphor materials, achieving both high conversion efficiency and high chemical stability remains challenging [5–7]. Instead, many researchers have focused on improving the characteristics of conventional phosphor materials based on YAG, nitride, or silicate, by treatment with additional chemicals [8,9]. Among various published chemical modifications, a protective coating on the surface of phosphor particles appears promising because it tends to enhance the optical properties and chemical resistance of a phosphor [5,8–13]. In many reports,

protective coating of a phosphor has been achieved using a thin layer of transparent metal oxide, and with $\alpha$-$Fe_2O_3$, $Y_2O_3$, $SiO_2$, $TiO_2$, or $In_2O_3$ as a barrier layer [8–17]. However, there have been few papers to demonstrate enhancement of luminous efficiency and lifetime in phosphor-converted LED (pc-LED) devices fabricated with coated phosphor particles [8,9].

In this paper, we show that a thin indium oxide (Amorphous $In_2O_3$) layer can significantly improve the conversion efficiency and moisture resistance of a conventional silicate phosphor already widely adopted in pc-LEDs. The uniform $In_2O_3$ coating over the surface of the silicate phosphor particles can be achieved using a low-temperature sol–gel process in alcohol solvent. In order to assess the influence of plasma treatment of silicate phosphor particles [10], three different pc-LEDs (the reference phosphor, the $In_2O_3$-coated phosphor without any treatment, and the $In_2O_3$-coated phosphor after plasma treatment) were fabricated and their performance measured. Special attention was paid to luminous efficiency and reliability of the pc-LED packages prepared with silicate phosphors, under different surface-treatment conditions.

## 2. Experiment

The green silicate phosphor ($SrBaSi_2O_4:Eu^{2+}$, O2B20) with average size of 15 $\mu$m was purchased from Force4 Co. For the plasma treatment of phosphor particles, a lab-made dielectric barrier
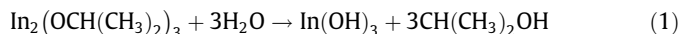
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discharge (DBD) plasma generator for use at ambient pressure was prepared [10]. Using Ar gas at a flow rate of 2slpm(standard liter per minute), stable plasma was obtained at input AC power of 20 W. For silicate phosphor particles, 20-min treatment showed the optimum result of the contact angle measurement (Phoenix, Surface Electro Optics Co.). To coat $In_2O_3$ onto the silicate phosphor particles, the low-temperature sol–gel reaction in alcohol solvent was selected. For the precursor of the sol–gel reaction, indium (III) isopropoxide (5% w-v isopropanol, Alfa Aesar) was prepared. To 50 ml of isopropanol (IPA, J.T. Baker) solvent, 2.5 ml of indium precursor solution, 0.5 μl of deionized water (DIW, Fisher scientific), and 5 g of silicate phosphor were added and stirred for 24 h at room temperature. To check the influence of plasma treatment on the performance of the phosphor, two coating-batches (bare phosphor and plasma-treated phosphor) were prepared and tested. Because indium isopropoxide is highly reactive in ambient air, the sol–gel coating process was performed in a $N_2$-filled glove box with $O_2$ content <5 ppm (mg/L). The coated phosphor particles were collected after filtering, and dried in a convection oven at 150 °C in order to evaporate solvent, for 10 min. The surface morphology, coating thickness, and elemental composition of the phosphor particles were analyzed using scanning electron microscopy (SEM, Hitachi S-4700), functional transmission electron microscopy with energy dispersive X-ray scattering (TEM/EDX, FEI TECNAI F20), and focused-ion-beam (FIB) high resolution SEM (Quanta™ 3D FEG). To measure the light absorption rate and the quantum efficiency of phosphors, we used the 'absolute photoluminescence quantum yield' measurement system (C10027/C9920-20, Bio-rad Co.). For this, 0.1 g of phosphor in a quartz holder was placed in an integrated sphere and a blue light (450 nm) was irradiated from a monochromator.

The pc-LEDs were fabricated using conventional GaN LED chips (Z900, $\lambda_{max}$ = 460 nm, Cree Co.) on a metal frame with the 5050 package (Point Engineering, Inc.). For the die adhesive layer, a conventional silver-loaded epoxy adhesive (T-3100, Sumitomo Chemical) was utilized [19,20]. Then, the fabricated devices were electrically connected using gold wires. To compare device-performance depending on the coating condition of the phosphors, three kinds of pc-LEDs (bare silicate phosphor: Device A, $In_2O_3$-coated phosphor without treatment: Device B, and $In_2O_3$-coated phosphor after plasma treatment: Device C) were prepared. For all devices, 20 wt% of corresponding phosphor particles were mixed with a silicone encapsulant (OE6630, Dow Corning). The metal frame was then soldered onto a metal PCB. After fabrication of the pc-LED package, the LEDs were characterized using a source meter (Keithley 2650) and a spectrometer system (CAS-140CT, Instrument System).

## 3. Results and discussion

The low chemical stability and low thermal stability of pc-LEDs have limited the reliability of the final lighting products incorporating them [20]. Due to these specific characteristics of the silicate phosphor, the experimental conditions under which the protective coating was applied to the silicate phosphor, also have to be carefully controlled. Previously, we showed that a silicate phosphor coated with a silicon oxide ($SiO_2$) layer had enhanced moisture resistance but the optical properties were degraded by damage resulting from the sol–gel coating process [8]. To prevent process-induced degradation, we adopted $In_2O_3$ sol–gel coating in IPA solvent using indium isopropoxide as a precursor [16]. In the $In_2O_3$ coating reaction, the hydrolysis step of indium iso-propoxide, and the successive polymerization step responsible for the formation of $In_2O_3$ sols, occurs as follows [16]:

$$In_2(OCH(CH_3)_2)_3 + 3H_2O \rightarrow In(OH)_3 + 3CH(CH_3)_2OH \quad (1)$$

$$2In(OH)_3 \rightarrow In_2O_3 + 3H_2O \quad (2)$$

After the polymerization reaction, two competitive reactions are possible (homogeneous nucleation and heterogeneous nucleation) [13,18]. The former can yield monomeric $In_2O_3$ particles in the solvent that are not favorable for the coating process. To achieve uniform coverage over the surface of the phosphor particles, heterogeneous nucleation is much preferable, resulting in $In_2O_3$ sols deposition on the phosphor surface and their participation in surface coating. It has been reported that the driving force of sol-deposition may be attributed to the adhesion of $H_2O$ molecules to phosphor particles, or to the surface-charge potential accumulated from other reactive sites on the phosphor surface [13,16].

To enhance the deposition rate of $In_2O_3$ sols to the phosphor surface, we utilized the conventional plasma treatment method to increase the surface-charge potential of the silicate phosphor. For practical reasons, the DBD Ar-plasma generator was used at ambient pressure for the treatment of these small particles. To analyze the change in surface energy of the phosphor particles after plasma treatment, we measured the contact angle of a water drop on a phosphor particle layer on a glass plate, secured with adhesive tape. Images in Fig. 1 shows the result of the contact-angle measurement. The plasma treatment decreased the contact angle from 46° to 16°. It seems that during the plasma treatment, many hydrophilic functional units like —OH or =O are normally generated on the surface of silicate materials. Although we utilized only 15 μm phosphor particles, the change of contact angle shows that the plasma treatment made the silicate phosphor surface hydrophilic, and increased the surface-charge potential.

After plasma treating the phosphor particles, $In_2O_3$ coating was performed. For the reference sample, we also prepared an $In_2O_3$ coated sample using the bare phosphor without plasma treatment. Fig. 2 shows the SEM and TEM images for the bare silicate phosphor, the $In_2O_3$-coated phosphor without any treatment, and the $In_2O_3$-coated phosphor after plasma treatment.

The conventional bare silicate phosphor had lots of cracks and a rough surface (Fig. 2a and b). After the sol–gel coating process, the cracks appeared to be filled with the $In_2O_3$ coating, resulting in a smoother surface than for the bare phosphor particle (Fig. 2c).
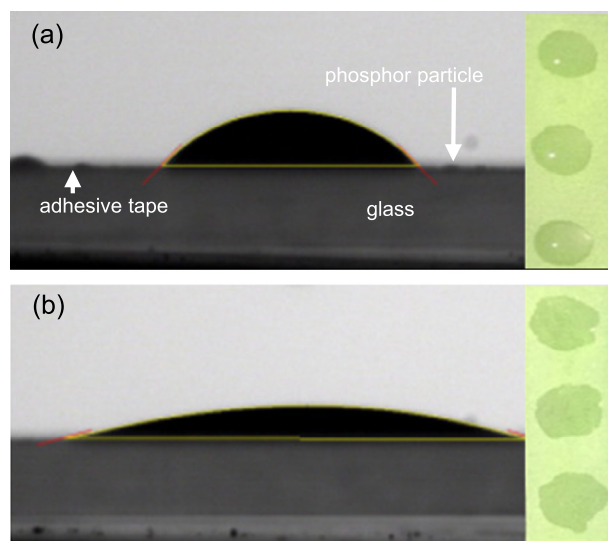


**Fig. 1.** Photographs of contact angle measurement using a water drop for (a) bare silicate phosphor and (b) plasma-treated silicate phosphor: The inset image is the top view of the tape-covered phosphor particle layer on glass plate after dropping the water.