Plasma assisted atomic layer deposition of Al_2O_3 coating phosphate-based phosphor powders for light emission diode

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Abstract: In this work, plasma assisted atomic layer deposition (PA-ALD) vibrating fluidized bed is built to deposit alumina as a barrier layer in highly hydrolysable phosphate-based phosphor powders. The coatings and their conformality are confirmed by scanning electron microscope and transmission electron microscope. It is concluded that PA-ALD Al_2O_3 is proper technique to protect the powders, and can efficiently block the humid permeation and prevent the powders from the hydrolysis.

Keywords: PA-ALD, Al_2O_3 coating, phosphate-based phosphor powders.

1.Introduction

The stability and luminescent property of phosphor powders have the crucial impact on the life and quality of light emitting diode (LED). Normally the red, green and blue, i.e. the three primary colors, are combined for LED lamp emitting a white light[1]. The red phosphor with orthophosphate as the matrix and doped with Eu^{2+}, Mn^{4+} for activator has potential in white light conversion LED applications benefiting to the low color temperature and the high color rendering index[3-4]. However, this powder is also sensitive to water. The strategic resolution is to cover the powder by a barrier layer forming a core-shell structure to improve the stability of the phosphor in the moist environment but not damaging the luminescent property.

In this work, we used plasma assisted atomic layer deposition (PA-ALD) and O_2 replaceing H_2O as oxidan to deposit Al_2O_3 as a barrier layer coating the phosphor powder surface to prevent the humid permeation. The proposal is to improve the device stability and to extend the working life.

2. Experiments

In our experiment, we adopted the vibrating fluidized bed to disperse powders during PA-ALD process[5]. The vibration system was driven by asymmetry motors, and the amplitude was tunable by adjusting vibration frequency. Owing to the vibration, the reactive gas fully contacted with the micro-size particles in the fluidization bed. During experiments, the vibration frequency of motor was set at 50 Hz.

In order to avoid the blockage of the transfer tube line, the precursor TMA and oxidant water were inputted to the reactive tube from the top and bottom of quartz tube, respectively.

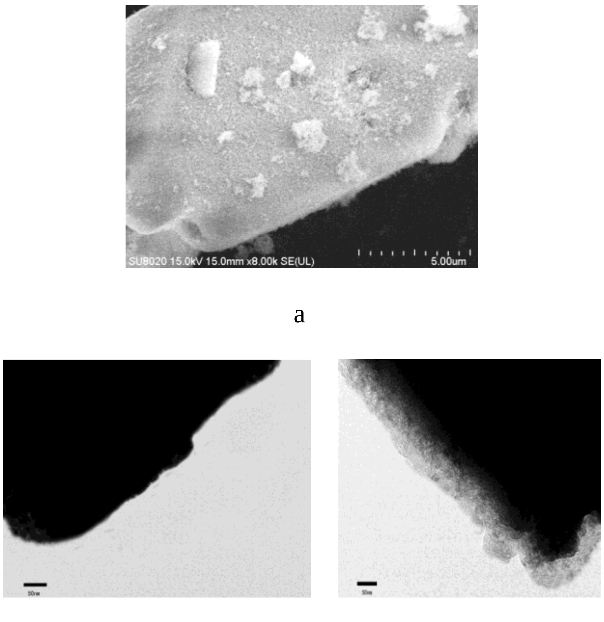
3. Results and discussion

Fig. 1(a) is SEM image of pristine phosphor powders. One can see that the particles consisted of big and small particles in irregular shape. There were lots of fluffy debris on the bar surface owing to the dusts formed during grinding.

TEM image in Fig. 1(c) clearly revealed the interface between Al_2O_3 and powders. The ~50 nm thickness of Al_2O_3 after 500 cycles of ALD contrasted with uncoated powder in Fig. 1(b). Al_2O_3 coatings were dense and conformal.

From Fig. 1(d) it is concluded that ALD process did not deform the powder shape, the bar-shape powder was still fluffy debris on surface after ALD Al_2O_3 process. From Fig. 1(f) SEM image we further concluded that coated particles were stable in the deionized water. The bar-shape particles with lots of fluffy debris on surface were identical to the previous sample even they were soaked in deionized water for 24 hours.

Comparing EDX mappings in Fig. 1(e) with (g) one can result that Al_2O_3 coatings did not spall the surface after soaked in the water. The uniform distribution of Al element on the particle surfaces claimed that not only the Al_2O_3 coating was uniformity on particle surface, but the immersing process did not wash the coating from the particle surface.



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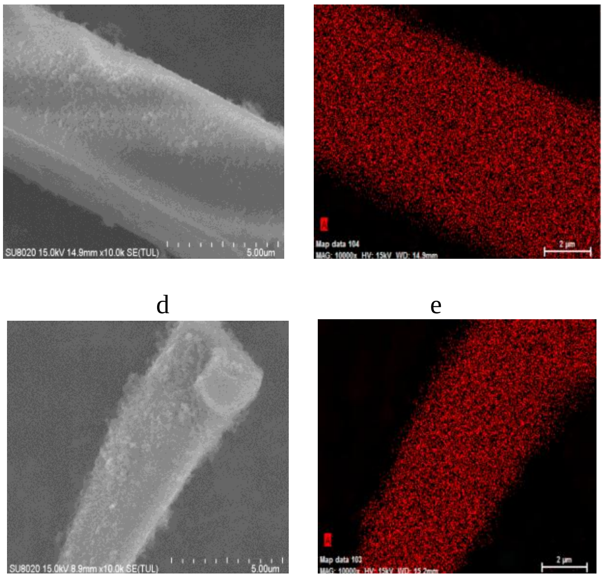

Fig.1 SEM and TEM images of phosphor powders and the distribution of the Al o phosphor; b-TEM image of uncoated powder (the scale bar is 50 nm); c- TEM image of 500 cycles of ALD Al_2O_3 coating powders (the scale bar is 50 nm); d-SEM image of coated phosphor powder before immersed in water; e-EDX mapping of Al in (d); f-SEM image of coated phosphor after soaked in water for 24 hours; g- EDX mapping of Al in (f)n the surfaces (a-SEM images of uncoated .

The barrier properties of Al_2O_3 coating were evaluated indirectly by immersing phosphor powders into deionized water and then measuring the variation of solution pH value, because the red phosphor of $Ca_9K(PO_4)_7$ is easily hydrolyzed in water and demonstrates an alkalinity. Fig. 2 shows that when uncoated powders were put into the water the solution pH value was jumped quickly and stabilized at pH=7.47, while for the alumina coating powders the pH value also rose remarkably but taking a long time to stability. Closer analysis, it is noticed that in pristine powders the rapid increase of pH value at the beginning took 60 min and then the stabilization needed 110 min; for ALD Al_2O_3 coating samples, it spent ~300 min for the stabilization of the solution pH value.

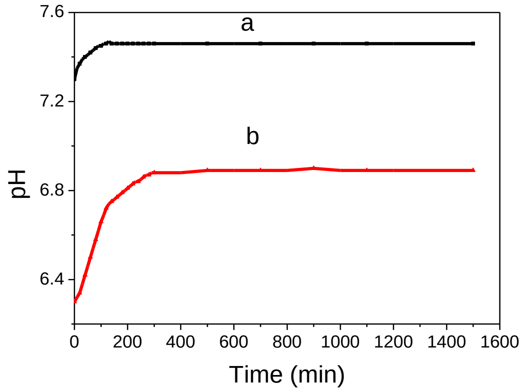

FIG.2 The variation of pH values versus immersing period. (a) uncoated powder; (b) 500 cycles of PA-ALD Al_2O_3coating powders

4. Conclusions

Al_2O_3 coating successively encapsulated the phosphate-based red phosphors in an PA-ALD vibrating fluidized bed. SEM and TEM images validated the dense and compact alumina coating on the powder surface. The Zeta potential also affirmed the existence of Al_2O_3 coating. PL results indicated that when the coating was in certain thickness the luminous properties of the powders were improved. We were then convinced that ALD technique can be very possibly applied in phosphate-based phosphor coverage to hamper the water permeation and to extend the light service life in future.

5.References

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