Efficiency improvement of solar cells by CaAlSiN$_3$:Eu$^{2+}$ and Y$_2$O$_3$:Eu$^{3+}$ phosphors

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Abstract: CaAlSiN$_3$:Eu$^{2+}$ (CASN) and Y$_2$O$_3$:Eu$^{3+}$ (YO) phosphors are mixed into ethyl vinyl acetate (EVA) to form luminescence down-shifting (LDS) films which are used to improve crystalline silicon solar cells by converting the photons with the wavelength from 200 nm to 500 nm into red light. Experimental results show that the conversion efficiency of the solar cells is enhanced from 19.61% to 20.00%. The improvement is better than that with only CASN phosphors in EVA films. The reason is the high quantum yield of YO phosphors in the wavelength range 250 nm - 350 nm, which offsets the poorer performance of CASN phosphors in this wavelength range.

1. Introduction

Although the conversion efficiency of solar cells has been continuously increasing in recent years [1-2], they are still suffering the decrease in the performance after packaging because of the increased surface reflection and the absorption in the encapsulation materials [3-5]. Luminescent down shifting (LDS) materials doped into encapsulation materials is considered to be a possible way to improve this problem [6]. Although the quantum yield of LDS materials is less than 1, they can still enhance the efficiency of solar cells by converting short wavelength photons into longer wavelength photons to which the solar cells have better response [7].

Lots of LDS materials have been investigated for solar cells and can be separated into three main categories: quantum dots, organic dyes and rare-earth phosphors [8-10]. Compared with quantum dots and organic dyes, rare-earth phosphors are the most applicable LDS materials for the solar cells due to their large Stokes shift (>200 nm), high quantum yield and low cost [11].

Many researchers have applied LDS phosphors on the solar cells. Although the performance of the cells are improved, these phosphors have limited effect because their narrow excitation band [12-15]. The CaAlSiN$_3$:Eu$^{2+}$ (CASN) phosphors have wider excitation band and emit red light where the crystalline silicon (c-si) solar cells exhibit a better response, so it is a good candidate for solar cells [16-17]. However, the quantum yield of CASN phosphors become lower (< 50%) below 300 nm, which restricts the improvement of the solar cells.

In this work, we choose the Y$_2$O$_3$:Eu$^{3+}$ (YO) phosphors which have high quantum yield (∼ 100%) below 300 nm to offset the poor performance of CASN phosphors in the wavelength range below 300 nm [18]. We introduce the mixture of CASN and YO phosphors into ethylene vinyl acetate (EVA) to form LDS films which are used to encapsulate the solar cells. This process is similar to that of production lines and convenient to be applied in photovoltaic industry. To make a comparison, we also make EVA films with only CASN phosphors and EVA films without any phosphor.
2. Experiment

The CASN and YO phosphors are purchased from Grirem Advanced Materials Company, and the c-si solar cells (the size is 2 cm X 2 cm) are provided by Maodi Solar Technology Company. The LDS films with CASN and YO phosphors were prepared as follows. The EVA, CASN phosphors, YO phosphors were mixed according to the mass ratio of 1: 0.015: 0.015 ratios. After that, the mixture was heated to 180°C, and then pressed into the films with the thickness of 0.3 mm in a vacuum chamber. The LDS films with only CASN phosphors was made through the similar procedure, where the mass ratio is EVA: CASN=1:0.015. Then, the LDS films, single c-si solar cells and glasses were packaged together in a vacuum chamber of 0.1 Pa and at temperature 160°C. The schematic structure of the modules is shown in Figure1.

![Figure 1. Schematic structure of the solar cell modules with CASN and YO phosphors](image)

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of CASN and YO phosphors were measured by Ocean Optics MAYA 2000PRO. The absorption of films were tested by SHIMADZU UV-1780. Qtest Station 2000AD produced by Crowntech is used to measure the external quantum efficiency (EQE) and the surface reflectivity of the solar cells. Two light sources, tungsten lamp and deuterium lamp, are used in combination to scan the wavelength range 200-1100 nm. The conversion efficiency was tested by IEC AAA XJCM-9 (GSolar).

To demonstrate the effects of the CASN and YO phosphors on the solar cells, three c-si solar cells have been intentionally selected. The three cells have similar short circuit currents (Jsc), open circuit voltages (Voc), fill factors (FF) and conversion efficiency (ƞ). Three packaged solar cells are: the sample S1 does not include any phosphor, the sample S2 includes only CASN phosphors and the sample S3 includes CASN and YO phosphors.

3. Results and discussion

Figure 2 shows the normalized photoluminescence excitation (PLE) and photoluminescence (PL) spectra of CASN, YO phosphors. The CASN phosphors have a broad excitation band from UV region to 590 nm and emits the light with the peak around 605 nm, which is a typical 5d-4f transitions of Eu²⁺ [19]. While, because of 5D0 → 7F2 transitions within Eu³⁺, the YO phosphors exhibits luminescent properties with nearly 100% QE [20]. These results indicates that the mixture of CASN and YO phosphors has an excitation band which is wide enough to cover the low response band of the solar cells.

The performance of the bare solar cells and the packaged cells are summarized in Table 1. In order to reduce the measuring errors, the parameters of each sample have been measured for six times and the average values are given in Table 1. It can be noted that Voc and FF are kept nearly unchanged before and after packaging. The conversion efficiency of S1 (without phosphor) is 19.38%, lower than 19.58% of its bare cell (the relative growth is -1.02%). The conversion efficiency of S2 (with CASN phosphors) increases from 19.62% of the bare cell to 19.86% of the packaged cell (relative growth is 1.22%), and the relative growth of S3 (with CASN and YO phosphors) is 1.98%. Clearly, the introduction of CASN and YO phosphors gives a best improvement of the solar cells.

To explain these experimental results, the EQE and the reflection of the cells are measured, as shown in Figure 3. For the packaged cells, the EQE is slightly increased and the reflection is decreased in the region of 300-400 nm after packaging. This is because packaged cell has the structure of
air-glass-EVA-cells which forms an index gradient and reduces the reflection in the short wavelength range[21-22]. In the middle and long wavelength ranges, the reflectivity of packaged cells increases and their EQE is lowered slightly. These results agree well with previous reports [23-24].

Figure 2. (a) Normalized photoluminescence excitation (PLE) spectra of CASN and YO phosphors monitored at 605 nm and 610 nm, respectively. (b) Normalized photoluminescence (PL) spectra for CASN and YO phosphors excited by 450 nm and 254 nm, respectively.

Figure 3. (a) External quantum efficiency. (b) Reflectivity of solar cells

By comparing packaged cell of S1 (without phosphor) and S2 (with CASN phosphors), it can be seen that the introduction of CASN phosphors brings a rise in the conversion efficiency by 2.24% relatively. This can be explained by the LDS effect of the CASN phosphors. The CASN phosphors absorb the short lights in the range of 250-500 nm and produce red emission peaking at 605 nm and lower the reflection.

As for the packaged cell S3 (with CASN and YO phosphors), its increase in the conversion efficiency is larger than that of S2 (with CASN phosphors). The introduction of YO phosphors improve the packaged cells through two possible mechanisms: one is that YO phosphors increase the absorption of the light in the range of 250-300 nm; other is that YO phosphors scatter the light of 300-500 nm, which increases the absorption of the light by CASN phosphors.
Table 1. Performance parameters of bare cells and packaged cells.

| Sample | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | $\eta$ (%) | $\Delta J_{SC}$ (%) | $\Delta \eta$ (%) |
|--------|----------------------|--------------|----|------------|----------------------|------------------|
| S1     | Bare Cell            | 38.62        | 0.655 | 0.77       | 19.58                | -1.17            |
|        | EVA on Cell          | 38.17        | 0.656 | 0.77       | 19.38                | -1.02            |
| S2     | Bare Cell            | 38.62        | 0.653 | 0.77       | 19.62                | 1.19             |
|        | EVA + CASN on Cell   | 39.08        | 0.654 | 0.77       | 19.86                | 1.22             |
| S3     | Bare Cell            | 38.64        | 0.654 | 0.77       | 19.61                | 2.25             |
|        | EVA + CASN +YO on   | 39.51        | 0.654 | 0.77       | 20.00                | 1.98             |

4. Conclusions
This paper proposes a method for improving the efficiency of crystalline solar cells by using CaAlSiN$_3$:Eu$^{2+}$ (CASN) and Y$_2$O$_3$:Eu$^{3+}$ (YO) phosphors. The YO phosphors improve the luminescence down-shifting effect of CASN phosphors in the wavelength range below 300 nm and increasing the absorption. Although introduction of the YO and CASN phosphors brings higher reflection, the improved spectral response results in a slight increase of the energy conversion efficiency from 19.61% to 20.00%.

5. References
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