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Broadband $Cr^{3+}/(Pr^{3+}/Yb^{3+})$ quantum cutting down-conversion system doped in $Y_2O_3/Y_3Al_5O_{12}$ heterostructure thin film

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ABSTRACT

In this work, granular $Y_2O_3/Y_3Al_5O_{12}$(YAG) heterostructure thin films with 100–200 nm holes on surface were fabricated by depositing metal yttrium on c-plane sapphire and subsequent thermal anneal. Such Y_2O_3/YAG thin films are excellent matrix for luminescent materials based on rare earth. Based on this matrix, a $Cr^{3+}/(Pr^{3+}/Yb^{3+})$ broadband down-converter was fabricated for improving the photovoltaic conversion efficiency of crystalline silicon solar cell (c-Si SC). Cr^{3+} was used to harvest the incident light and sensitize Pr^{3+}/Yb^{3+} quantum cutting (QC) couple. QC down-conversion to Yb^{3+} infrared emission was realized in the region of 230 nm to 500 nm, which approaches the maximum bandwidth of QC down-conversion for c-Si SC.

1. Introduction

Crystalline silicon solar cell (c-Si SC) shows a low conversion efficiency when the incident sunlight wavelength is less than 500 nm [1]. The thermalization of excess energy and electron-hole recombination near surface are responsible for the poor quantum yield. It could be overcome by introducingdown-conversion process [2–6]. Quantum cutting (QC) down-conversion, which can convert one high-energy photon into two low-energy photons by using the Ln^{3+}–Yb^{3+} (Ln = Tb, Tm, Pr, Er, Ho, Nd, etc.) couple systems has been widely studied. However, the forbidden f–f transitions of the trivalent lanthanide ions limit the width of the absorption band of the phosphors. Some semiconductors (such as ZnO, ZnSe, CdSe, and $Cd_{1-x}Zn_xS$) [7–10] and several ions with 4f–5d transition (such as Ce^{3+}, Eu^{2+}, Yb^{2+}, and Bi^{3+}) [11–14] have been used as sensitizers with broadband absorption. For Pr^{3+}–Yb^{3+} couple, the QC down-conversion processes can take place upon excitation of Pr^{3+} into the $^3P_{0,1,2}$,$^1I_6$ levels and subsequent energy transfer (ET) from Pr^{3+}: $^3P_0$ energy level to two Yb^{3+} acceptors with Pr^{3+}: $^1G_4$ acting as the intermediate level. It can even provide quantum yield close to 200% via resonant ET from Pr^{3+} to Yb^{3+} [4–6]. Unfortunately, the absorption band of Pr^{3+}/Yb^{3+} QC couple mainly sits in the region of UV band with $\lambda < 350$ nm due to the parity-forbiddance of $4f^n \rightarrow 4f^n$ transitions in Pr^{3+}. How to broaden the QC absorption band to wavelength of 500 nm is the key to practical applications for Pr^{3+}/Yb^{3+} QC couple. Introducing a sensitizer with broadband absorption is an easy solution for this problem. To ensure a high-efficient ET, the sensitizer should also have matching level with Pr^{3+} ion. Cr^{3+} is such a sensitizer for Pr^{3+}/Yb^{3+} QC couple that meets the above two requirements. The spin-allowed $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ transitions of Cr^{3+} can harvest the energy over a broad range of 250–700 nm, and efficient ET in Cr^{3+}/Yb^{3+} and Cr^{3+}/Pr^{3+} couples have been demonstrated by many experiments [15–18]. On the other side, the choice of hosts is also important. Wide bandgap oxides containing Yttrium with high transparency, high refractive index, and relatively low phonon energy, such as Y_2O_3, $Y_3Al_5O_{12}$ (YAG), $YAl_3(BO_3)_4$ (YAB), have been investigated as host materials for luminescent materials based on rare earth for a long time [11–13,15,16,19–22]. Some luminescence processes, such as two-photo absorption, can be partly tuned by the size of Yttrium oxides

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matrix [19]. In this current paper, Cr^{3+} ion was chosen as the sensitizer of Pr^{3+}/Yb^{3+} QC couple. A granular Y_2O_3/YAG heterostructure thin film with nanoholes was used as the matrix for the $Cr^{3+}/(Pr^{3+}/Yb^{3+})$ QC system. A continual absorption band for QC down-conversion was constructed from 230 to 500 nm. Because the near infrared (NIR) emission at about 1000 nm from the broadband down-converters meets the maximum spectral response of silicon devices, it is expected to boost the energy conversion efficiency of c-Si SC.

2. Experimental details

Y–Al–O compounds and $Cr^{3+}/(Pr^{3+}/Yb^{3+})$ co-doped $Y_2O_3/Y_3Al_5O_{12}$ heterostructure thin films with about 200 nm thickness were fabricated, where the Y–Al–O compounds can include Y_2O_3, $Y_4Al_2O_9$ (YAM), $YAlO_3$ (YAP), and $Y_3Al_5O_{12}$ (YAG). First, Yttrium or (Y/Cr/Pr/Yb) metal films were deposited on c-plane sapphire substrate by multi-target magnetron co-sputtering. Yttrium, ytterbium, praseodymium, and Cr_2O_3 targets with 4 N purity were used as the precursors. Ar gas with 5 N purity was used as the sputtering gas. H_2 gas with 5 N purity was mixed into Ar to provide a reducing atmosphere. The H_2/Ar flow ratio was 3%. The deposition temperature and the chamber pressure were kept at 500 °C and 0.5 Pa during the sputtering. Next, the deposited metal thin films were oxidized in oxygen atmosphere at 500 °C for 3 h, and then were annealed at high temperatures in oxygen atmosphere and/or in vacuum ($<3 \times 10^{-3}$ Pa).

The crystal structure of the samples were characterized by X-ray diffraction (XRD) in theta–2theta scanning mode on a Bruker AXS D8 advance diffractometer (40 KV, 40 mA) with Cu Kα radiation ($\lambda = 0.15405$ nm). The X-ray photoelectron spectra (XPS) were carried out on a VG ESCALAB 250 Electron Spectrometer with a monochromatic Al Ka X-ray source (1486.6 eV) at 12 kV and 20 mA, and the pressure in the chamber was maintained at 10^{-7} Pa or lower during data collection. The C 1s neutral carbon peak at 284.6 eV was used as the reference for all binding energies. The morphology was studied by using a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 5 or 3 kV. The photoluminescence (PL) and PL excitation (PLE) spectra were measured on an FLSP 920 spectrofluorometer. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(A) shows the XRD patterns of the samples. Besides diffraction peaks from Y_2O_3 and sapphire substrate, some other peaks appear in the patterns. Because the samples grown on sapphire experienced a high-temperature annealing, thermal diffusion and solid state reaction are unavoidable near the interface between Y_2O_3 thin film and sapphire substrate. The inset in Fig. 1 sketches the formation processes of Y–Al–O compounds. As shown by curve (a), for the thin film annealed at 1000 °C for 9 h, besides a intense (400) diffraction peak from Y_2O_3, some weaker diffractions not belonging to Y_2O_3 phase appear in the pattern. By comparing with PDF cards, these peaks are assigned to (012), (122), and (032) diffractions from $Y_4Al_2O_9$ (YAM), respectively. For the thin film annealed at 1250 °C for 9 h, the YAM (−223) peak increases markedly and shows a comparable intensity with the (400) peak of Y_2O_3, concomitantly, diffractions from $YAlO_3$ (YAP) phase also began to appear in the pattern, as shown by curve (b). For the thin film annealed in oxygen atmosphere at 1300 °C for 9 h and then vacuum annealed at 1050 °C for 3 h, YAG phase appears, and the Y_2O_3 and YAG diffractions dominate the XRD pattern. The intensity of (211) and (422) diffractions from YAG is comparable with the Y_2O_3 (400) peak, as shown by curve (c). Increasing the vacuum annealing time to 6 h, the XRD pattern is dominated by (211), (420), and (422) peaks of YAG, as shown by curve (d). With further increasing annealing temperature in oxygen atmosphere, for example, 1500 °C for 9 h, the thin film is also dominated by YAG phase, but almost all the doped Cr ions escape out of the thin film. As seen, with the develepment of the solid phase reaction, the Al/Y atomic ratio in the Y–Al–O compounds increases gradually.

The XPS measurements were carried out to determine the chemical composition of these samples. Fig. 1 (B) shows the XPS spectra of Y3d peaks of the samples experienced different annealing processes. For the sample only annealed in oxygen atmosphere at 1000 °C, the peaks centered at 156.7 eV and 158.3 eV correspond to Y $3d_{5/2}$ and $3d_{3/2}$ in Y_2O_3, respectively. For the sample annealed in oxygen atmosphere at 1300 °C and then vacuum annealed at 1050 °C for 6 h, which has almost converted into YAG, the binding energy of Y $3d_{5/2}$ and $3d_{3/2}$ shift to 157.8 and 159.8 eV correspondingly. For comparison, the XPS spectrum of the sample annealed in oxygen atmosphere at 1300 °C and then

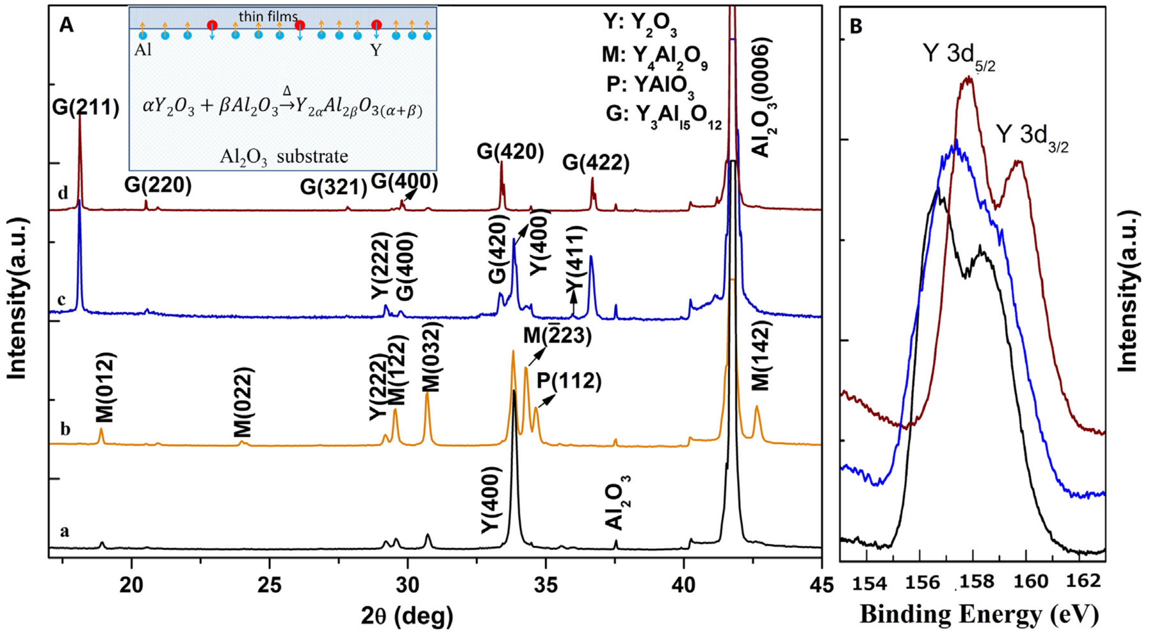

Fig. 1. (A): XRD patterns of samples. The peak at 2θ = 41.68° is from sapphire (0006) diffraction. (B) XPS spectra for Y3d of samples annealed in different conditions.