

High Conversion Efficiency Photovoltaic Cell Enhanced by Lanthanide Complex Phosphor Film Coating

Tetsuro Jin, Satoshi Inoue, Shuji Tsutsumi, Ken-ichi Machida,* and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita Osaka 565

(Received October 7, 1996)

Maximal outputs of amorphous silicon (a-Si) photovoltaic cells (PVC) coated by the organically modified silicate (ORMOSIL) composite film containing a terbium bipyridine complex were increased to be 8% higher than those of the uncoated a-Si PVC, owing to the effective optical modulation from UV to visible light by the lanthanide complex incorporated into the ORMOSIL matrix.

It is known that the photoactive lanthanide ions such as Eu^{3+} and Tb^{3+} form stable crystalline complexes with heterocyclic ligands, *e.g.* bipyridine (bpy) and phenanthroline (phen), which exhibit efficient energy transfer from the coordinated ligands to the chelated lanthanide ions.¹⁻³ A potential application feasibility of these compounds is based on the fact that the organic portion of molecules can absorb ultraviolet radiation and they provide sharp green line emissions with good efficiency via the subsequent intramolecular energy transfers.

On the other hand, silicon solar cells are the most promising materials for the energy conversion of sunlight to electric power, but, in the case of a-Si PVC, the light transformation efficiency in UV region is significantly lower than that in visible one. The spectroscopic sensitivity curve of a-Si solar panel provides an absorption edge in the shorter wavelength region at about 300 nm, and furthermore the light intensity in this region is much lowered by additional absorption of the resin film coated practically for protection. Consequently, the sunlight fractions at the shorter wavelength are completely wasted in such PVC system. However, if the UV lights are converted to the visible ones which are sensitive for a-Si PVC by efficient photoluminescent materials, one can expect a considerable enhancement in the PVC conversion efficiency. Indeed, $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ provides strong line emissions and the main line of them is peaking at 545 nm, which is very close to the peak of sunlight spectrum (550 nm).^{5,6}

In this study, the silica-based ORMOSIL composite matrices, which have been prepared and characterized as suitable host materials for organic compounds such as dyes⁷⁻⁹ and lanthanide complexes,¹⁰⁻¹³ are synthesized by sol-gel method and $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ and incorporated into them. Furthermore, hybrid solar cell devices are fabricated by coating with the resulting ORMOSIL composite materials on the surface of a-Si solar cell panels and their conversion characteristics of sunlight to electric power were studied.

The lanthanide complex and ORMOSIL matrices used here have been prepared according to the procedure reported elsewhere.¹¹⁻¹³ The viscous gel solutions of ORMOSIL composite materials containing various amounts of $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ were coated on the surface of commercially available a-Si PVC (TDK Co., Ltd.) panels, which consisted of p-i-n structure of Si and covered with polyester laminate film, and dried at room temperature for the duration more than 38 h in air. The excitation and emission spectra of the resulting terbium complex

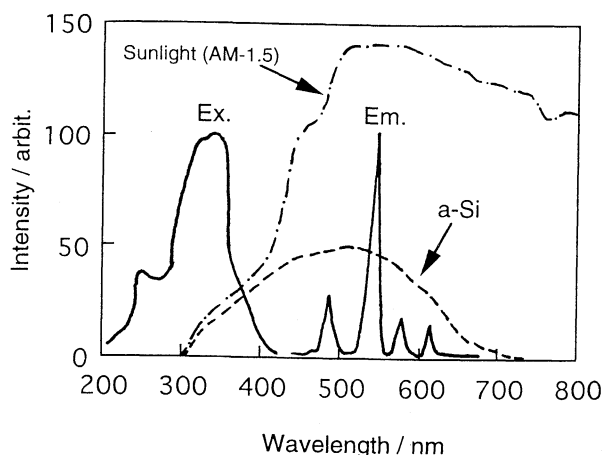


Figure 1. Typical excitation and emission spectra of the ORMOSIL composite material doped with $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ (solid line). The dotted and dashed lines represent the usual sunlight spectrum and the spectroscopic sensitivity curve of a-Si solarcell, respectively.

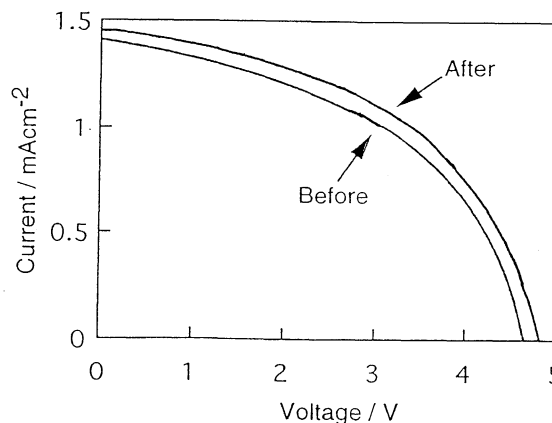


Figure 2. V-I characteristics of an a-Si PVC devices obtained under the same condition of modulated sunlight irradiation with the surface before and after surface coating with the ORMOSIL: $[\text{Tb}(\text{bpy})_2]^{3+}$ composite film (thickness = ca. 0.1 mm). The illuminated area was about $4.0 \times 6.5 \text{ cm}^2$.

incorporated into ORMOSIL matrix (ORMOSIL: $[\text{Tb}(\text{bpy})_2]^{3+}$) were measured by the procedure described previously.¹¹ Measurements of the V-I characteristics for the hybrid a-Si PVC devices were carried out on a solar simulator with xenon lamp (100 mWcm^{-2}) and the deep UV lights below 300 nm were cut by a glass filter. The enhancement in the electric outputs of the hybrid a-Si PVC devices were evaluated in comparison with those of the non-coated a-Si PVC.

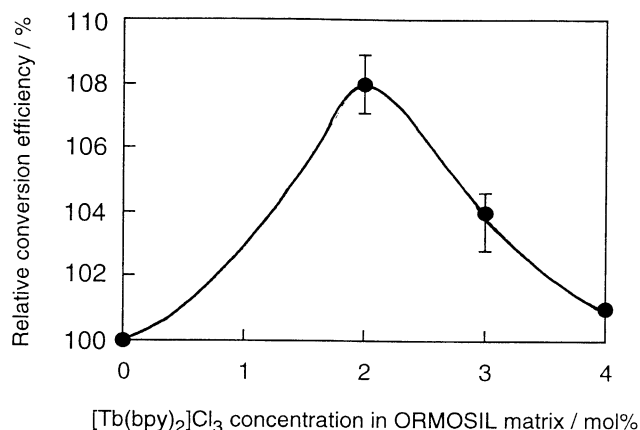


Figure 3. Complex concentration dependence of the relative conversion efficiency for the hybrid a-Si PVC devices with ORMOSIL:[Tb(bpy)₂]³⁺ composite film.

Excitation and emission spectra of the ORMOSIL composite material containing 2 mol% of [Tb(bpy)₂]Cl₃ as dried at 323 K are shown in Figure 1, together with the spectroscopic sensitivity curve of the commercial a-Si PVC. In this case, the excitation (absorption) spectrum of lanthanide complex gave a strong band peaking at ca. 310 nm, which was attributed to the $\pi - \pi^*$ transition of bpy ligands, followed by the intense line emissions in the visible region via the energy transfer from the ligands to Tb³⁺ ions. However, the absorption spectrum pattern of ORMOSIL:[Tb(bpy)₂]³⁺ was kept at the background level in the visible region sensitive for the a-Si PVC. These results indicate that the ORMOSIL:[Tb(bpy)₂]³⁺ composite film is suitable as an optical modulator to enhance the electric outputs of a-Si PVC. Because the sunlight fraction in the UV region as is insensitive for the PVC is effectively converted to the useful visible lights by the terbium complex.

The V-I characteristics of the hybrid a-Si PVC devices coated with the ORMOSIL composite material film were measured, together with those of uncoated a-Si ones (see Figure 2). The complex concentration dependence of the relative conversion efficiency obtained under the same irradiation condition is shown in Figure 3. The efficiency was maximized at the dopant concentration of 2 mol%, of which the hybrid device provided the further enhancement up to be around 8%. However, the reflectivity measured on the hybrid a-Si PVC device was ca. 7% higher than that of non-coated PVC in the region from 330 to 800 nm. In practice, the preliminary experiments demonstrated that the maximal output might be enhanced to be 20% higher than that of the uncoated a-Si PVC by optimizing the chemical composition between the silica and organosilane. Also, the

luminescence characteristics of ORMOSIL:[Tb(bpy)₂]³⁺ composite materials are strongly dependent on the coating conditions, film thickness, and subsequent heat treatment conditions. Further experiments are now in progress by considering the above factors.

Conclusions drawn in the present study are as follows:

- (1) The maximal outputs of a-Si PVC is effectively enhanced by simple coating of the ORMOSIL composite materials incorporated with the terbium complexes which can convert from the UV light to the visible ones as photoemissions.
- (2) The conversion efficiency is strongly dependent on the coating film conditions of ORMOSIL:[Tb(bpy)₂]³⁺ and, by optimizing these conditions, the efficient value around 8% is obtained.

The authors wish to acknowledge Profs. S. Yanagida and H. Okamoto for their assistances to measure the V-I characteristics of a-Si PVC. The authors also would like to thank TDK Co., Ltd. for supplying a-Si PVC. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" Nos. 06241106 and 06241107 from the Ministry of Education, Science, Sports, and Culture of Japan.

References

- 1 N. Filipescu, S. Bjorklund, N. McAvoy, and J. Degnan, *J. Chem. Phys.*, **48**(7), 2895 (1968).
- 2 S. P. Sinha, *J. Inorg. Nucl. Chem.*, **28**, 189 (1966).
- 3 S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).
- 4 H. J. Hovel, R. T. Hodgson, and J. M. Woodal, *Sol. Energy. Mater.*, **2**, 19 (1979).
- 5 K. Kawano, J. Tominaga, H. Satoh, R. Nakata, and M. Sumita, *Jpn. J. Appl. Phys.*, **29**, L319 (1990).
- 6 R. Nakata, N. Hashimoto, and K. Kawano, *Jpn. J. Appl. Phys.*, **35**, L90 (1996).
- 7 E. T. Knobbe, B. Dunn, P. D. Fuqua, and F. Nishida, *Appl. Opt.*, **29**, 2729 (1990).
- 8 R. Reisfeld, D. Brusilovsky, and M. Eyal, *Proc. Photo-Opt. Instrum. Eng.*, **1182**, 230 (1988).
- 9 D. Avnir, V. R. Kaufman, and R. Reisfeld, *J. Non-cryst. Solids*, **74**, 395 (1985).
- 10 L. R. Matthews and E. T. Knobbe, *Chem. Mater.*, **5**, 1697 (1993).
- 11 T. Jin, S. Tsutsumi, Y. Deguchi, K. Machida, and G. Adachi, *J. Electrochem. Soc.*, **142**, L195 (1995).
- 12 T. Jin, S. Tsutsumi, Y. Deguchi, K. Machida, and G. Adachi, *Alloys & Compd.*, in press (1996).
- 13 T. Jin, S. Tsutsumi, K. Machida, and G. Adachi, *J. Electrochem. Soc.*, in press (1996).
- 14 V. N. Saxena, *Indian J. Pure & Appl. Phys.*, **21**, 306 (1983).