Influence of zinc phthalocyanines on photoelectrical properties of hydrogenated amorphous silicon[*]

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Abstract: Composites consisting of hydrogenated amorphous silicon (a-Si: H, inorganic) and zinc phthalocyanine (ZnPc, organic) were prepared by vacuum evaporation of ZnPc and sequential deposition amorphous silicon via plasma enhanced chemical vapor deposition (PECVD). The optical and electrical properties of the composite film have been investigated. The results demonstrate that ZnPc can endure the temperature and bombardment of the PECVD plasma and photoconductivity of the composite film was improved by 89.9% compared to pure a-Si: H film. Electron mobility-lifetime products $\mu\tau$ of the composite film were increased by nearly one order of magnitude from 6.96×10^{-7} to 5.08×10^{-6} cm^2/V. Combined with photoconductivity spectra of the composites and pure a-Si: H, we tentatively elucidate the improvement in photoconductivity of the composite film.

Key words: zinc phthalocyanines; a-Si:H; photoconductivity; mobility-lifetime product
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1. Introduction

Composites of inorganic and organic, which combine the desired properties of both the organic and inorganic components, are particularly interesting materials in the photovoltaic research field. Some organic dye molecules are excellent light absorbers from the visible region to the near infrared (IR)[1]. Zinc phthalocyanine (ZnPc), as an environment friendly material[2] with high thermal stability[3], is one such candidate[4] with an absorption coefficient about 10^5 cm^{-1} [5,6]. However, the carrier mobility of ZnPc is very limited due to rapid recombination[7]. Silicon thin film, on the other hand, shows good transport properties for carriers but relative low absorption compared with ZnPc in the visible light region.

Earlier, amorphous silicon has been reported[8] as being sensitized by bromoindium phthalocyanine. Recently, Mayer *et al.*[9] reported that ZnPc could be incorporated into amorphous Si as a sensitizer. Later they showed[10−12] that the photoconductivity of μc-Si film increased by 15% under white light illumination and proved ZnPc be an effective photosensitizer for μc-Si: H film, which is valuable work.

In this paper, we find that the photoconductivity of the composite film is improved considerably compared to pure a-Si: H film. The improvement in photoconductivity is explained by sensitization of a-Si: H by ZnPc and probable improvement of transport properties in composite film. In addition, the microstructure of a-Si: H in the composites does not change compared to its counterpart from Raman spectra. We also demonstrate that ZnPc can endure the temperature and bombardment of the PECVD plasma.

2. Experiment

The composite film was composed of two layers: ZnPc and a-Si: H. The composite was fabricated as follows. Firstly, films of ZnPc were deposited on substrate at ambient temperature. Subsequently, a-Si: H films were deposited by radio frequency (RF) PECVD on the as-prepared ZnPc films.

ZnPc powder ($\geqslant$ 97% purity) purchased from Aldrich was sublimated from an Al$_2$O$_3$ crucible, which was heated by tungsten filament to 250 °C. The α-form structure[13] ZnPc film was deposited on Corning 7059 glass at room temperature in a vacuum of 1.5×10^{-3} Pa.

The deposition conditions of the a-Si: H films were an RF power of 5 W, a deposition pressure of 70 Pa, a substrate temperature of 170 °C and a flow of pure silane (6 sccm) diluted in hydrogen, respectively. The chamber pressure ($P_{\rm r}$) was adjusted by a throttle valve.

All films were deposited on Corning 7059 glass for optical and electrical measurements. The thickness of a-Si: H film was around 220 nm, determined interferometrically after dep-

Table 1. Photoconductivity (σ_{Ph}), dark conductivity (σ_D), product $\mu\tau$ and photosensitivity of pure a-Si:H and the composite film.

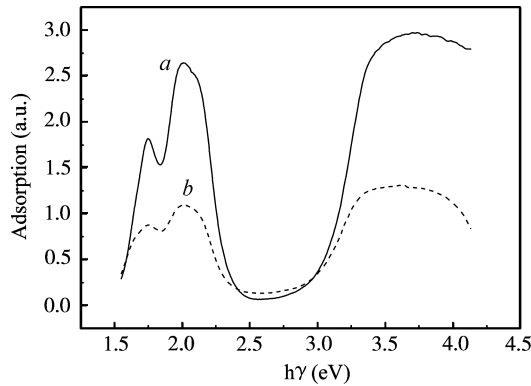| Sample	σ_{Ph} (S/cm)	σ_D (S/cm)	$\mu\tau$ (cm^2/V)	Photosensitivity
a-Si:H film	4.35×10^{-4}	6.96×10^{-8}	6.96×10^{-7}	$6.25 \times 10^{+3}$
Composite film	8.26×10^{-4}	2.34×10^{-8}	5.08×10^{-6}	$3.53 \times 10^{+4}$

Fig. 1. Absorption spectra of (*a*) pure ZnPc film and (*b*) the blue layer, which was obtained by removing the a-Si: H layer from the composite film deposited on glass substrate.

osition. The thickness of the as-deposited ZnPc film was around 230 nm, determined by a surface profiler (Tencor 10-03000). Absorption spectra were obtained using a Hitachi U-3010 spectrophotometer. All the electrical measurements were performed along the film plane, with coplanar aluminum contacts separated by 0.4 mm. The photo and dark conductivity of the films were measured under a vacuum of 10^{-1} Pa and a Keithley 6485 picoammeter was used for the measurements. Photoconductivity was studied under white light of intensity 100 mW/cm^2 by a water-filtered beam from a halogen lamp. Steady-state photocurrent measurement was applied for electron carrier mobility-lifetime product ($\mu\tau$) with red light (670 nm) to ensure uniform absorption and carrier generation[14]. The microstructure of the samples was investigated from Raman backscattering studies at room temperature by a microscopic confocal Raman spectrometer (Renishaw RM2000), using 514.5 nm photons from an Ar$^+$ laser source.

3. Results and discussion

Stability of ZnPc during the composite fabrication process is one of the fundamental prerequisites for the preparation of the composite film. Hence, we investigated whether there would be any ZnPc left after being subjected to high temperature and bombardment by PECVD plasma. a-Si: H film in the composites was removed and left a blue layer. Figure 1 shows the comparison of absorption spectra between the blue layer and pure ZnPc. As can be seen from this figure, both spectra exhibit two peaks located at 1.75 eV (exciton transition[15] or vibrational interval[16]) and 2.00 eV ($\pi - \pi^*$, a_{1u}–e_g)[17], respectively. This shows the similarity between the blue layer and ZnPc. On the other hand it is reported that ZnPc binding energy is –5.66 eV[18] while the typical electron temperature in PECVD plasma is around 2 eV[19] (less than 5.66 eV),

which suggested that the ZnPc would not be decomposed by PECVD plasma. Sadaoka *et al.*[3] reported that ZnPc would not decompose even at 300 °C. However, the substrate temperature used for our samples deposition is below 200 °C (lower than 300 °C), demonstrating that ZnPc would not be thermally disintegrated during the sample fabrication process. Thus we concluded that the blue layer is ZnPc film, which had kept its integrity, either physically or chemically, in the composite film fabrication process.

The typical electronic properties of pure a-Si: H film and its corresponding composite film are shown in Table 1. We note three different points: (1) photoconductivity (σ_{Ph}) of the composite film was increased, compared with pure a-Si: H film. (2) Electron mobility-lifetime products $\mu\tau$ of the composite film were enhanced by nearly one order of magnitude from 6.96×10^{-7} to 5.08×10^{-6} cm^2/V, which reflects the fact that photogenerated carrier transport in the composite was improved. (3) Dark conductivity was lower and photosensitivity was higher when the composite film is compared to pure a-Si:H .

To explore which part of incident light contributes to the sensitization of a-Si: H by ZnPc, we measured the photoconductivity spectra of the samples as shown in Fig. 2. From this figure, the high value of the photoconductivity spectra of the composite film between 1.60 and 2.02 eV is a clear indication of the sensitization of a-Si: H by ZnPc. Photon energy of effective incident light for the sensitization ranges from 1.60 to 2.02 eV.

The phenomena above observed in Fig. 2 can be explained as follows. It is known that there are two types of photo-generated exciton in organic material[13]. One is the Wannier-Mott (WM) exciton, and the other is the Frenkel (F) exciton. The WM exciton is formed by an electron photoexcited from the valence band to a position near the bottom of the conduction band and is tightened by a hole in the valence band through weak coulombic interaction. So the energy to form a WM exciton is nearly equal to the energy gap of organic material (1.94 eV for ZnPc[20]). Therefore, we attributed the excitons photogenerated in ZnPc by incident light with energy in 1.94–2.02 eV (B band in Fig. 2) to the WM excitons. The F exciton is generated by an electron from the valence band to a metastable state, which is located in the energy gap. The excited electron on the metastable state is more close to the valence band than its counterpart in the WM exciton. Thus, we ascribed the exciton photogenerated in ZnPc by a photon in 1.60–1.94 eV (A band in Fig. 2) as an F exciton. As a result, we can easily see from Fig. 2 that the sensitization is mainly due to Frenkel excitons, which were photogenerated on ZnPc
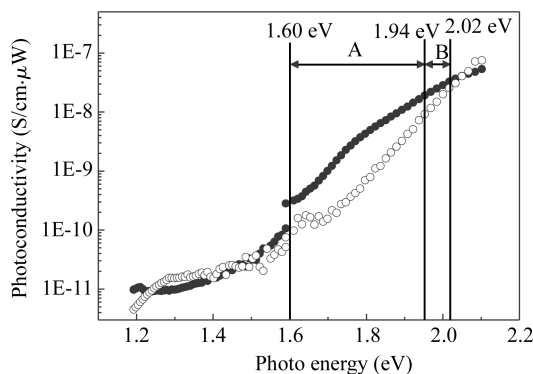
Fig. 2. Photoconductivity spectra of pure a-Si:H (open circles) and composite film (solid circles). The excitons photoexcited by photons in band A are assigned to Frenkel excitons and those in band B are assigned to Wannier-Mott excitons.
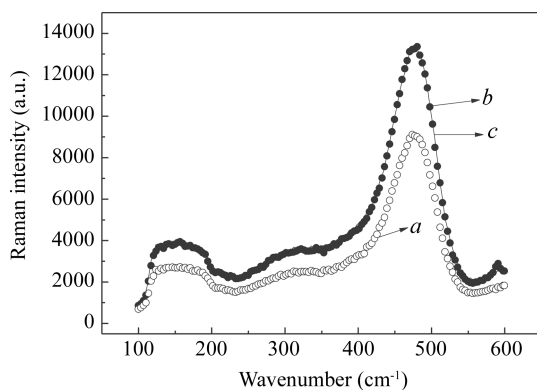

Fig. 3. Raman spectra of the a-Si: H film (*a*, open circles) and the composite film (*b*, solid circles). Spectrum (*c*, solid line) was obtained by normalizing spectrum (*a*).

then diffused to the a-Si: H/ZnPc interfacial area. The excitons on the interfacial area were separated by a built-in electrical field, which points from a-Si: H to ZnPc, producing a charge-separated state with an excessive electron drifting onto the a-Si: H and a hole moving onto the ZnPc. The excessive electron on the a-Si: H was collected and thus contributed to the photoconductivity improvement of the composite film.

Some reports[21, 22] showed that the substrates had an influence on the spatial distribution of the microcrystalline/amorphous phases with film as deposited. Is it possible that the improvement of conductivity in Table 1 is due to the increase of microcrystalline phases in the composites? Raman spectra of the composites and its corresponding pure silicon film were measured and shown in Fig. 3. From this figure, both Raman spectra of the pure a-Si: H (*a*) and the composite film (*b*) exhibit typical amorphous silicon features[23]. Spectrum (*c*) is obtained by normalizing spectrum (a) as follows. The spectrum (*a*) data was multiplied by 1.465, which was derived from the value of the 480 cm^{-1} peak in spectrum (*b*) divided by its counterpart in spectrum (*a*). According to Ref. [24], the peak at 480 cm^{-1} was assigned to the transverse-optical band, which is considered an important parameter for measuring the short range order. From Fig. 3, we can see that spectrum (*c*) could be regarded the same as spectrum (*b*) within experimental error. This fact shows that the existence of ZnPc on substrate

did not change the microstructure of a-Si: H film from Raman measurement. Thus, the improvement of photoconductivity in Table 1 is not due to the increase of microcrystalline phases.

In addition, Wagner *et al.*[25] reported that electron mobility μ of amorphous silicon and microcrystalline silicon are 1 and 50 cm^2/(V·s), respectively. From Table 1, electron mobility-lifetime products $\mu\tau$ of the composite film were improved by nearly one order of magnitude. Since the μ is not changed due there being no microcrystalline phase increase, the improved $\mu\tau$ indicated that the lifetime τ of photogenerated carriers in the composites was longer than its counterpart in the pure a-Si: H. Thus, it is suggested that carrier transport properties are improved, which also could contribute to the photoconductivity of the composite film.

4. Conclusion

In summary, composite film was fabricated by vacuum evaporation of ZnPc and sequential deposition of a-Si: H via PECVD. We found photoconductivity of the composite film was increased greatly compared to pure a-Si: H film. Electron mobility-lifetime products $\mu\tau$ of the composite film were increased by nearly one order of magnitude from 6.96×10^{-7} to 5.08×10^{-6} cm^2/V, which suggested that transport properties in the composites were enhanced. In addition, we demonstrated that ZnPc molecules could keep their integrity in the whole composite film fabrication process and the microstructure of a-Si: H in the composites did not change compared to its counterpart from Raman spectra. The improvement of conductivity is due to excessive electron drift from ZnPc onto a-Si: H.

In the next step, the composite material will be optimized and integrated into solar cell devices.

Acknowledgements

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