Photothermal Spectroscopy by Atomic Force Microscopy on Crystalline Silicon Solar Cell Materials

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1. Introduction

A solar cell is one of key devices as renewable energy sources and the following three primary losses should be reduced to improve the solar cell performance: (1) transmission of light with photon energy below bandgap of solar cell material, (2) excess energy emission as heat from photo-generated electrons and holes in relaxation process down to conduction and valence band edges, respectively, and (3) internal recombination of photocarriers. The former two factors can be controlled through bandgap engineering of solar cell materials, while the last one strongly depends on the material quality. In a Si material, especially, most recombination processes are nonradiative because Si is an indirect gap material. Since the nonradiative recombination process generates heat, we can expect that the nonradiative recombination property will be investigated through a precise measurement of thermal expansion. To realize such a measurement, we have already proposed the photothermal (PT) spectroscopic measurement by atomic force microscopy (AFM), in which the periodical photothermal expansion produced by intermittent light illumination is locally detected by an AFM cantilever, and combined it with the dual sampling (DS) method to improve its sensitivity [1]. Up to now, we observed the PT signals around a grain boundary in a multicrystalline Si material [2], and we found that the PT signal was significantly influenced by the surface recombination in addition to the recombination at the grain boundary [3]. In this study, we mainly focused on the surface recombination and compared the PT signals on single crystalline Si materials with and without the surface treatment by hydrofluoric acid (HF), by which the Si surface is chemically stabilized owing to hydrogen termination [4].

2. Experimental

Figure 1 shows our experimental setup for the PT spectroscopy based on a commercial AFM system (SII NT, SPA-300HV/SPI4000). Our AFM was operated in the intermittent contact mode in nitrogen gas, and all measurements were performed at room temperature. To avoid the influence of stray light, a Si piezoresistive cantilever (SII NT, PRC-DF40P) was used. Its spring constant, resonant frequency, and quality factor at the resonance were typically 40 N/m, 450 kHz, and 600, respectively. The sample surface was illuminated by monochromatic light from a tunable Ti:Al₂O₃ laser in the



Fig.1 Experimental setup for PT spectroscopy by AFM with the dual sampling (DS) method [1].

continuous wave mode, whose intensity and spot diameter were about 100 mW/cm² and >1mm at the sample surface, respectively. This incident light was periodically modulated by an optical chopper with a duty ratio of 50%, and the modulation frequency was 540 Hz. The output of cantilever deflection sensor was sampled by the DS circuit, and the PT signal was acquired as the periodical change in the DS circuit output at the modulation frequency extracted by the lock-in amplifier [1].

The samples used in this study were single crystal Si solar cells fabricated on a p-type substrate of 300 μ m in thickness with a phosphorus doped n-type surface layer with or without the surface treatment by HF vapor for one minute followed by a rinse with purified water.

3. Results and discussion

Figure 2(a) and (b) show the AFM topographic images of the single crystalline Si solar cells without the HF treatment and with it, respectively. As shown in this figure, surface flatness was improved by the HF treatment. In addition, we can suppose that the native oxide at the Si surface was removed by this treatment.

Figure 3 shows the incident photon energy dependence of PT signal measured on both samples. The result indicates that the PT signals on the HF treated sample were apparently reduced. One possible cause of this reduction is the decrease of the light intensity penetrating into the sample due to the increase of surface reflection resulting from the improvement of the surface flatness as observed in the AFM topography. However, we have experimentally confirmed that the intensity of the reflected light at the sample surface was almost independent of the surface treatment, and therefore we can exclude this possibility. On the other hand, the penetration depth of the incident light at a photon energy of 1.57 eV was estimated to be 11 μ m, and the heat generation by the surface recombination should strongly contribute to the enhancement of the PT signal in our experimental conditions. Consequently, the reduction of the PT signal on the HF treated sample is well attributable to our expectation that the heat generation caused by the surface recombination is well suppressed by this treatment.

This figure also indicates that the PT signal slightly increased as an increase of the photon energy of the incident light in both cases. We consider that this tendency is well related with the minority carrier diffusion length in the solar cell material, which is normally investigated by the surface photovoltage measurements [5,6]. The slopes of the PT signal as a function of the photon energy obtained in these two samples were almost the same, and this result is very consistent with an interpretation that the slope is dominated by the diffusion length as a bulk property, but not the surface property.

4. Conclusions

We have performed the PT spectroscopy by AFM on the single crystalline Si solar cell materials with and without the HF treatment on the surface, and discussed the influences of the surface recombination as well as the minority carrier diffusion length on the PT signals. As a result, the reduction of the PT signal owing to the suppression of the surface recombination and the incident photon energy dependence of the PT signal related with the minority carrier diffusion length were observed, which indicates a capability of the PT spectroscopy by AFM to analyze the surface property as well as the bulk property in the solar cell materials.

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Fig.2 Topographic images of single crystalline Si solar cells (a) without HF treatment and (b) with HF treatment. The average roughness (Ra) is (a) 0.71 nm and (b) 0.44 nm.



Fig.3 Incident photon energy dependence of PT signals. Dotted and chain lines are fitting lines calculated by the least square method.