Journal of Non-Crystalline Solids 358 (2012) 2319–2323

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Localized surface plasmon enhanced microcrystalline–silicon solar cells

Jakapan Chantana *, Yanqiu Yang, Yasushi Sobajima, Chitose Sada, Akihisa Matsuda, Hiroaki Okamoto

Graduate School of Engineering Science, Osaka University, Machikaneyama-cho 1–3, Toyonaka, Osaka 560-8531, Japan

ARTICLE INFO

Article history:
Received 3 August 2011
Received in revised form 10 December 2011
Available online 7 January 2012

Keywords:
Localized surface plasmon;
Silver nanoparticles;
Hydrogenated microcrystalline silicon;
Solar cell;
Light trapping

ABSTRACT

A novel type of substrate named “Ag–SP substrate”, in which silver nanoparticles are incorporated, is introduced and utilized as a back reflector for hydrogenated microcrystalline-silicon solar cell in a substrate-type (n-i-p) configuration. Optical and morphological analyses of Ag–SP substrates fabricated with various sizes of silver nanoparticles are systematically performed. It is shown that silver nanoparticles in Ag–SP substrate structure can lead to significant scattering of light when their diameter increases up to 300 nm. Furthermore, the photocurrent of the solar cell fabricated on an Ag–SP substrate with RMS roughness as small as 16.5 nm and a proper lateral diameter (approximately 300 nm) of silver nanoparticles is improved as compared to that of the solar cell prepared on reference textured substrate with RMS roughness of 25.3 nm, owing to strong scattering of light by silver nanoparticles in the red-infrared region.

1. Introduction

Hydrogenated microcrystalline-silicon (μc-Si:H) thin films prepared by plasma-enhanced chemical vapor deposition (PECVD) are promising materials for various applications in optoelectronic devices, since μc-Si:H shows high stability under light-soaking conditions and high absorption of light in the near infrared region of the solar spectrum as compared to hydrogenated amorphous silicon (a-Si:H) [1–9]. When considering the application in μc-Si:H-based solar cells, light trapping plays an indispensable role in enhancing the photocurrent and efficiency. This is because μc-Si:H has low optical absorption coefficient in the visible range of the solar spectrum due to its indirect band gap [4,7-10]. In general, μc-Si:H-based substrate-type (n-i-p) solar cell allows one to design and fabricate its light trapping schemes before the deposition sequence of the silicon based layers at low temperature, thus offering more flexibility in the choice of fabrication methods [9]. Light trapping method for efficient light absorption using textured substrate with high surface roughness has been utilized as one of the most useful techniques [5,7,9-10]. However, it has been frequently experienced that the photovoltaic performance of μc-Si:H n-i-p solar cells deteriorates by using highly textured substrate due to i) defective grain-boundary formation [10], and/or ii) poor surface coverage of p-type μc-Si:H layer [11,12]. Therefore, a novel back reflector with strong scattering (diffusing) of light to enhance optical path in an intrinsic μc-Si:H active layer, as well as small surface roughness to avoid the deterioration of photovoltaic performance, is needed.

Localized surface plasmon (LSP) refers to collective electron charge oscillations in metallic nanoparticles that are excited by light [13,14]. It has recently attracted interest due to the wide range of applications, such as surface-enhanced Raman spectroscopy [15], chemical and biological sensing [16], etc. Collective electron charge oscillations lead to a resonance interaction between incident light and metallic nanoparticles, resulting in a strong scattering of incident light.

In this work, we propose a new type of substrate named “Ag–SP (surface plasmon) substrate”, where silver nanoparticles (Ag NP) bring about scattering of light, for a back reflector in μc-Si:H n-i-p solar cell fabricated at high rates (>2 nm/s). The changes in the optical properties and surface morphology of Ag–SP substrates prepared with various sizes of Ag NP are investigated. Finally, we demonstrate the improvement in the photocurrent of the solar cell in the long wavelength region through the application of an Ag–SP substrate as compared to a reference textured substrate.

2. Experimental

First, experimental studies on light scattering of Ag NP in the simplest sample structures, Glass/Ag NP and Glass/ZnO:Al/Ag NP, were carried out. The next step was to propose a new Ag–SP substrate, utilized for light trapping in the μc-Si:H n-i-p solar cell. The configuration of the Ag–SP substrate was Glass/Ag (100 nm thick)/ZnO:Al (50 nm thick)/Ag NP/ZnO:Al(25–100 nm thick). The Ag layer and transparent conductive oxide (TCO) layer of Al-doped ZnO (ZnO:Al) were deposited by radio-frequency (RF: 13.56 MHz) magnetron sputtering. The Ag NP layer was obtained by thermal evaporation of a thin silver (Ag) layer and subsequent annealing treatment. The thickness of the thin Ag layer was varied from 11 to 34 nm. Annealing temperature was changed from 250 to 500 °C. ZnO:Al layer, covering on Ag

---

* Corresponding author. Tel.: +81 668506317; fax: +81 668506316.
E-mail address: jakapan@semi.ee.es.osaka-u.ac.jp (J. Chantana).

0022-3093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.12.038

NP, was also fabricated by RF magnetron sputtering. For comparison, reference textured substrate with root-mean-square (RMS) roughness (σ_{RMS}) of 25.3 nm was prepared, whose structure was Asahi type-U SnO_2 glass/Ag (100 nm thick)/ZnO:Al (100 nm thick).

The optical transmittance and reflectance of substrates were measured by scanning spectrophotometer (UV-3100PC, Shimadzu) using spherical integrator (ISR-3100, Shimadzu). Reflectance HAZE (R-HAZE) is defined as a ratio of diffuse reflectance (R_d) to total reflectance (R_t). In Ag–SP substrates and the reference textured substrate, their absorptance is given as $(100-R_t)$ %, since they are not transparent due to the thick Ag layer (100 nm). Due to low absorption coefficient of μc-Si:H, weakly absorbed light in the long wavelength region, 600 to 1000 nm, has to be strongly scattered and reflected on the back reflector of μc-Si:H n-i-p solar cell [4,7-10]. Averaged total reflectance (averaged R_t), and averaged R-HAZE were taken in the long wavelength region, 600 to 1000 nm, in which incident light passes through 2 μm thick i μc-Si:H and reaches the light diffusing Ag–SP back-reflector. The surface morphology was obtained from topographic images taken by atomic force microscopy (AFM; SPA400/SPI3800N, Seiko Instruments). The mean lateral diameter of Ag NP was evaluated from the height–height correlation function obtained from AFM images [17]. The Ag–SP substrates have an almost constant sheet resistance, as low as 2.32×10^{-1} Ω/□, measured by the four-point probe method (MCP-T600, Mitsubishi Chemical Corporation).

Finally, in order to compare the photovoltaic performance of μc-Si:H n-i-p solar cells fabricated on Ag–SP substrate and on reference textured substrate, two solar cell structures were prepared. The structure of the Ag–SP cell on Ag–SP substrate was Glass/Ag/ZnO:Al/Ag NP/ZnO:Al/n-i-p/TCO/Ag-grid. The structure of the reference cell on reference textured substrate was Asahi type-U SnO_2 glass/Ag/ZnO:Al/n-i-p/TCO/Ag-grid. Phosphorus-doped n-type μc-Si:H and boron-doped p-type μc-Si:H were prepared by RF-PECVD, while an intrinsic μc-Si:H active layer with the thickness of 2 μm was deposited at high rate (2.3 nm/s) using VHF-PECVD [18]. The InTiO and ZnO:Al layers were used as front TCO. After the formation of the top Ag-grid, the solar cell was thermally annealed in N_2 atmosphere at 200 °C for 1 h. The active area of the solar cell is 0.23 cm^2. The cell parameters, short-circuit current (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (*FF*), were evaluated from the current–voltage characteristics under Air Mass 1.5 illumination (100 mW/cm^2). External quantum efficiencies (QE) were measured using a conventional lock-in detection system. Photocurrent enhancement for Ag–SP cell is given as a ratio between external quantum efficiency of Ag–SP cell and that of the reference cell.

3. Results

3.1. LSP scattering effect on silver nanoparticles (Ag NP)

We have performed experimental studies on light scattering in the sample structures, (a) Glass/Ag NP and (b) Glass/ZnO:Al/Ag NP, in which Ag NP is well isolated. Fig. 1(a) and (b) show specular transmittance (T) and total reflectance (R_t) spectra of (a) and (b) sample structures. T and R_t spectra of both samples exhibit a complementary change and localized surface plasmon resonance wavelengths (λ_{SRP}) of Ag NP at 444 and 522 nm, as demonstrated in Fig. 1(a) and (b), respectively. Incident light at λ_{SRP} is strongly scattered, which is implied by the large overlap between dip in T and peak in R_t spectra. Furthermore, the shift of λ_{SRP} found between (a) and (b) sample structures is indicative of "surrounding media effect", which apparently demonstrates the scattering wavelength tunability. The experimental observation has provided the evidence of strong light scattering due to LSP scattering effect on Ag NP. Motivated by this observation, we have introduced Ag–SP substrate, in which light is scattered by Ag NP, so as to obtain a new type of substrate with strong scattering of light, as well as small σ_{RMS} for μc-Si:H n-i-p solar cell.

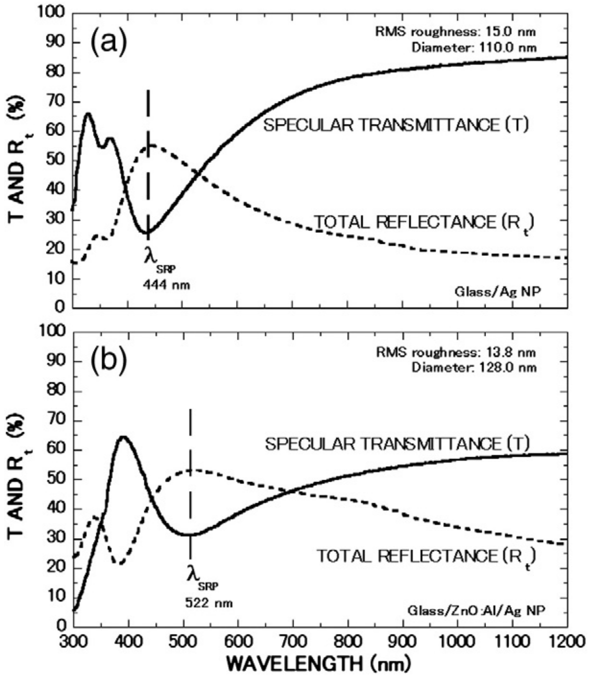

Fig. 1. Specular transmittance (T) and total reflectance (R_t) spectra of Ag NP corresponding to thin Ag layer thickness of 13 nm in the structures: (a) Glass/Ag NP, and (b) Glass/ZnO:Al/Ag NP. (λ_{SRP}: localized surface plasmon resonance wavelength).

Fig. 2 shows AFM topographic images of bare Ag NP on Glass/Ag/ZnO:Al under different formation conditions of Ag NP. Left figures show 3-dimensional views of AFM images, while right figures display top views of AFM images. The σ_{RMS} is proportional to the diameter of well-isolated Ag NP as observed in Fig. 2(a) and (b). The diameter of Ag NP (232 nm) in Fig. 2(b) is larger than that (110 nm) in Fig. 2(a), corresponding to thin Ag layer thickness of 22 and 13 nm, respectively. Moreover, a reduction in areal density of Ag NP is observed ("lower" coverage ratio of Ag NP) with an increase in diameter of Ag NP. This obviously demonstrates that the manipulation of size and density of Ag NP on Glass/Ag/ZnO:Al is feasible through the adjustment of formation conditions of Ag NP.

Fig. 3(a) and (b) depict R-HAZE and R_t spectra in Ag–SP substrates under different formation conditions of Ag NP, while Fig. 3(c) illustrates the spectra of the reference textured substrate. We performed a simple optical simulation in the Ag–SP substrate structure, Glass/Ag/ZnO:Al (50 nm thick)/Ag NP/ZnO:Al(25–100 nm thick), in which different optical patterns were observed, depending on the thickness of ZnO:Al layer (not shown). Therefore, the optical structures in R-HAZE spectra in Fig. 3 are caused primarily by optical interference effect in ZnO:Al layer, which conceals the characteristic LSP resonance features. Furthermore, the increase in R-HAZE and the decrease in R_t, related to absorptance by $(100-R_t)$ %, in both Ag–SP substrates are observed in the long wavelength region as compared to those in a reference textured substrate. In other words, the presence of Ag NP in Ag–SP substrates can lead to both scattering and absorption of light, where the sum of scattering and absorption is defined as the extinction of light by Ag NP [13,19-20]. With an increase in Ag-NP diameter from 156 to 360 nm, as shown in Fig. 3(a) and 3(b), the enhancement of R-HAZE and R_t is observed. As can be evidently seen, averaged R-HAZE, and R_t increase from 0.65 to 0.83 and from 39.5 to 54.8%, respectively. The result implies that incident light is more scattered and less absorbed on Ag–SP substrates with an increase in Ag–NP diameter.

Fig. 4(a) and (b) show averaged R_t and R-HAZE in various Ag–SP substrates and the reference textured substrate, plotted as a function of σ_{RMS}. It is demonstrated that the Ag–SP substrate with σ_{RMS} as low as 16 nm, corresponding to Ag–NP diameter of about 300 nm, and