Photocurrent characteristics of nanostructured thin films consisting of surface-modified silicon nanoparticles

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Abstract. We have studied optical and electrical properties in thin films consisting of the network of silicon nanoparticles modified with mercaptosuccinic acid (MSA). A photocurrent measurement system was set up to observe the photocurrent signal as functions of excitation photon energy and power. In addition, we observed the absorption spectra of the thin film and solution of the nanoparticles to clarify the contribution of the nanoparticles structure to the optical transition property. It was found that the photocurrent has an excitation-energy dependence while the profile is different from that of a bulk silicon photodiode. This behaviour suggests the specific photogenerated-carrier transport originating from the structure of the thin film of MSA-modified silicon nanoparticles.

1. Introduction

Semiconductor nanoparticles have attracted considerable attention in fundamental semiconductor physics and functional materials. A thin film consisting of a network of nanoparticles enables us to control transport properties of optically- and electrically-injected carriers[1,2], which is promising to develop novel electric and optoelectronic devices. Moreover, the carrier transport process in a subpicosecond range is sensitive to the structure of the thin film because the length of the carrier motion is comparable to the nanoparticle size and interparticle spacings[3]. This characteristic is beneficial in the development of terahertz optoelectronic devices[4].

A silicon nanoparticles (SiNPs) thin film has a great advantage in technological and economical aspects. There are numerous reports on the optical and electrical properties in SiNPs thin films while most of the studies were conducted in the structure consisting of SiNPs embedded in a silicon oxide[3]. The investigation of various structures of the SiNPs thin film is essential to the comprehensive understanding. Recently, Sato et al. fabricated thin films consisting of SiNPs surface-modified with a thin functional group using a mechanochemical process. This fabrication method enables us to produce various nanoparticles environments by selecting the modifier, which is expected to bring out a new functionality of the SiNPs thin film. In fact, the thin film consisting of the SiNPs modified with a short chain carboxylic acid, mercaptosuccinic acid (MSA), exhibits a distinct transport property of electrically-injected carriers[5].

In this work, we studied transport property of photogenerated carriers in the thin film consisting of the MSA-modified SiNPs at various photoexcitation conditions. We set up a photocurrent measurement system to observe the photocurrent signal as functions of excitation photon energy and...
power, and discussed the photocurrent response from the aspect of the structure of the MSA-modified SiNPs thin film.

2. Experimental

MSA-modified SiNPs were produced by wet grinding of the silicon powder in MSA-containing super dehydrated methanol using a planetary ball mill[5]. The average diameter of the SiNPs was estimated to ~20 nm by a scanning electron microscope; The quantum size effect is not expected in the diameter[6]. The thin film was fabricated by a drop casting process of the SiNPs dispersed in distilled water to a glass plate. For the electrical characterization, the droplet was deposited on a SiO₂ film with Au electrodes separated by a distance of 5 μm (The gap area was 5×600 μm²). In measurements of current-voltage characteristics, the light source was a laser diode with a photon energy of 1.9 eV. In measurements of the excitation energy dependence of the photocurrent signal, the light source was produced by the combination of a Xe lamp and a single monochromator with a spectral resolution of ~7 nm. The excitation light was focused around the electrode gap region by using an objective lens. Moreover, the reflected and scattered excitation lights by the sample surface were monitored using a CMOS camera to optimize the light focusing. The intensity of the excitation light was below ~1 μW to suppress a saturation behaviour of the photocurrent as described later. In addition, the excitation light was chopped by 5 Hz to detect the photocurrent signal by using a lock-in amplifier. The schematic view of the optical setup is shown in Fig. 3(a). All the measurements were conducted at room temperature.

3. Results and Discussion

The solid curves in Fig. 1 show the absorption spectra in the solution and thin film of the MSA-modified SiNPs. The offset profile of that in the thin-film sample is attributed to the scattering of the excitation light by a textured sample surface. The absorption spectra consist of a gradually increasing comportment that is similar to the spectrum in a bulk silicon[7] and a peak structure at ~2.5 eV. Such a peak structure is not observed in the SiNPs modified with ethoxy or propoxy groups fabricated by the same process (not shown here). Moreover, as shown by the dots in Fig. 1, the absorption in a MSA solution is negligible in the present energy range. Thus, the peak structure is specific to the MSA-modified SiNPs.

Figure 2 shows the current-voltage characteristics under the light illumination and dark conditions in the thin-film sample using the 1.9 eV-laser diode with the excitation power of ~3 mW.
The photocurrent signal that corresponds to the difference between the two curves is clearly seen at the applied bias voltage above ~3 V (6 kV/cm). The behaviour indicates that the transport process of photogenerated carriers is enhanced above ~3 V, because the number of photogenerated carriers is generally less dependent on the internal electric field.

To comprehensively evaluate the transport process of photogenerated carriers in the MSA-modified SiNPs thin film, we observed the photocurrent signal as functions of excitation photon energy and power using the optical setup shown in Fig. 3(a). Figure 3(b) shows the spectrum of the photosensitivity that is defined as the photocurrent value divided by the excitation power. The estimation of the photosensitivity is as follows. The inset in Fig. 3(b) shows the excitation-power dependences of the photocurrent value at the excitation photon energies of 1.8 and 2.5 eV. It is clear that the photocurrent values show saturation behaviours with an increase in excitation power. This behaviour is possibly attributed to reflect the volume of the nanoparticles in the electrode gap region. The dashed curves show the phenomenological fitted results using the equation of $I_{pc}(x)=A[1-\exp(-Bx)]$, where $A$ is a maximum photocurrent value and $B$ is a rate of the saturation. In the estimation of the photosensitivity, we assumed the slope of the fitting curve at the origin to the photosensitivity as shown by the lines. The estimated photosensitivity spectrum is increased with a decrease in photon energy, which will be discussed in the next paragraph. In addition, the spectrum has a periodical component with the period of ~0.28 eV. We confirmed that this periodical component disappears when the excitation light is defocused. Moreover, the observed peak wavelengths can be calculated by the equation of $\lambda_n=2L/n$, where $\lambda_n$ is the peak wavelength, $L$ is the gap distance that of 5 μm, and $n$ is an odd number. These facts suggest that the electrode gap structure is the origin of the periodical component; namely, the electrode gap structure affects the fluence of the excitation light to the SiNPs thin film.

As described in Fig. 3(b), the photosensitivity is increased with a decrease in photon energy. The rate of increase in photosensitivity from 3.0 eV to 1.5 eV is ~7. The rate is much higher than that of a bulk silicon photodiode, which is ~2 (Hamamatsu Photonics, S1336 series)[8]. The prominent near-infrared component in the present spectrum is attributed to the nature of the transport process in the network of the SiNPs nanoparticles; A similar spectral shape has reported in a SiNPs thin film[1]. Another possibility of the interpretation for the spectral shape is the contribution of sulfur atoms. A sulfur-doped silicon photodiode shows an enhancement of the photosensitivity in an infrared range, which is originated from optical transitions of sulfur-related states[9]. We note that sulfur is one of the element of MSA and the sulfur atoms are considered to couple to outermost silicon atoms in the MSA-modified SiNPs[5]. The contribution of the MSA modification is suggested also to the absorption spectra with the peak structures described in Fig. 1.

![Figure 2. Current-voltage characteristics under the light illumination and dark conditions in the MSA-modified SiNPs thin film. The energy and power of the excitation light were 1.9 eV and 3 mW, respectively.](image-url)
Figure 3. (a) Schematic view of the optical setup for the photocurrent measurement. (b) Photosensitivity spectrum in the MSA-modified SiNPs thin film under the applied bias voltage of 5 V (10 kV/cm). The inset shows the excitation-power dependences of the photocurrent value at the excitation photon energies of 1.8 and 2.5 eV. The dashed curves indicate the phenomenological fittings and the slopes of the solid lines correspond to the photosensitivities in a low excitation regime.

4. Summary
We have studied the optical and electrical properties of the thin film and solution of the MSA-modified SiNPs from the aspects of the absorption and photosensitivity spectra. The absorption spectra show the peak structure at ~2.5 eV, which is specific to the MSA modification. From the measurements of the photocurrent signals as functions of excitation power and photon energy and the consideration of the saturation behaviour, we precisely estimated the photosensitivity spectrum in the range from visible to near infrared. We found that the photosensitivity in the MSA-modified SiNPs thin film is further increased as approaching the near infrared range compared to that of a bulk silicon photodiode. The mechanism of the present transport process is attributed to the network structure of the nanoparticles or the additional optical transitions originating from sulfur-related states.

References
[1] Rezgui D B, Gourbilleau F, Maestre D, Palais O, Sibai A, Lemiti M and Brémond G 2012 J. Appl. Phys. 112 024324
[2] Gutsch S, Laube J, Hartel M A, Hiller D, Zakharov N, Werner P and Zacharias M 2013 J. Appl. Phys. 113 133703
[3] Němec H, Zajac V, Kužel P, Malý P, Gutsch S, Hiller D and Zacharias M 2015 Phys. Rev. B 91 195443
[4] Daghestani S N, Persheyev S, Cataluna A M, Ross G and Rose J M 2011 Sem. Sci. Technol. 26 075015
[5] Sato S, Dobashi T and Matsuda S 2015 Chem. Eng. J. 268 356
[6] Matsumoto T, Suzuki J, Ohnuma M, Kanemitsu Y and Masumoto Y 2001, Phys. Rev. B 63 195322
[7] Green A M 2008 Solar Ene. Mat. & Solar Cells 92 1305
[8] Hamamatsu.com, https://www.hamamatsu.com/us/en/product/type/S1336-8BQ/index.html
[9] Li C, Zhao J, Yu X, Chen Q, Feng J, Han P and Sun H 2017 IEEE Sens. J. 17 2367