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Effects of oxygen impurity on the energy distribution of gap states in hydrogenated amorphous silicon studied by post-transit photocurrent spectroscopy

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Oxygen is normally present in the highest concentration ($10^{18}-10^{20}$ cm^{-3} range) among the impurities in hydrogenated amorphous silicon (*a*-Si:H) and affects the electrical properties and light-induced changes in this material. However, little is known about how the energy distribution of trap states, $g(E)$, in undoped *a*-Si:H changes with the presence of oxygen. In this study, we prepare undoped *a*-Si:H samples in an ultrahigh-vacuum plasma-enhanced chemical-vapor-deposition chamber and intentionally introduce oxygen atoms at a concentration of 3×10^{19} cm^{-3} by adding CO_2 to the source gases. By comparing the results obtained for high-purity and oxygen-doped samples by post-transit photocurrent spectroscopy, we discuss the effects of oxygen on the energy distribution of electron and hole trap states before and after long exposure to light. It is found that the presence of oxygen atoms enhances the defect reactions during prolonged illumination, while the shapes of $g(E)$ in the as-deposited state are similar between the high-purity and oxygen-doped samples in the energy range studied (from $E_c-0.35$ eV to $E_c-0.65$ eV for electron traps and from $E_v+0.38$ eV to $E_c+0.78$ eV for hole traps). A light-induced decrease of the hole trap density in the energy range from $E_v+0.5$ to $E_v+0.75$ eV is observed and discussed.

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I. INTRODUCTION

It has been reported[1] that hydrogenated amorphous silicon (*a*-Si:H) contains a large amount of impurities, such as oxygen (O), nitrogen (N), and carbon (C), that are unintentionally introduced into the *a*-Si:H films during growth. The typical concentration of these impurities[1] is $10^{17}-10^{19}$ cm^{-3} for nitrogen and carbon and $10^{18}-10^{20}$ cm^{-3} for oxygen. The effects of these impurities on the electrical properties of *a*-Si:H films were discussed in the previous publications concerning impurities that had been intentionally introduced into the films at various controlled concentrations. Oxygen and nitrogen in undoped *a*-Si:H increase dark and photo conductivities[2–4] when their concentration exceeds 10^{19} cm^{-3}. The presence of oxygen deteriorates the characteristics of *a*-Si:H solar cells, which can be ascribed to the change in the electric field profile induced by the presence of oxygen.[3] These observations suggest that some oxygen and nitrogen atoms act as donors in undoped *a*-Si:H. On the other hand, Balberg *et al.*[5] suggested that oxygen may form acceptorlike states in undoped *a*-Si:H on the basis of a study on the thermal quenching of photoconductivity and the sensitizing effects. The presence of O, N, and C atoms also affects light-induced changes in *a*-Si:H. Kuwano *et al.*[6] pointed out that light-induced changes in solar-grade undoped *a*-Si:H films were considerably enhanced when the concentration of oxygen was increased from 2×10^{18} to 2×10^{19} cm^{-3}. They also suggested that defect states related to impurities can be formed below the midgap upon long exposure to light, in addition to light-induced Si dangling-bond states that were located around the midgap. Unold and Cohen[7] observed an increase in the light-induced changes in undoped *a*-Si:H when the carbon concentration was increased from 0.1 to 1 at. %. In spite of a considerable number of publications related to the effects of O, N, and C impurities on the properties of *a*-Si:H, there have been few reports on how these impurities affect the energy distribution of gap states, $g(E)$, in undoped *a*-Si:H. Although Kuwano *et al.*[6] and Balberg *et al.*[5] suggested the presence of impurity-related states below the midgap, they did not perform direct measurements of $g(E)$. Michelson and Cohen[8] reported the variation of $g(E)$ induced by oxygen, nitrogen, and carbon impurities. However, their *a*-Si:H films were phosphorus-doped *n* type and ion implantation was adopted to introduce the impurities. Therefore, it should be noted that $g(E)$ in undoped *a*-Si:H with the impurities introduced during film growth can be different from those reported by Michelson and Cohen.

In this paper, we study the effects of oxygen impurities on the energy distribution of gap states, $g(E)$, in undoped *a*-Si:H. We focus on oxygen since oxygen is normally present in the highest concentration among the impurities in *a*-Si:H, as mentioned above, and is the most difficult to reduce.[9] We employ post-transit photocurrent spectroscopy[10–13] (PTPS) to obtain $g(E)$. In PTPS, trap states are filled with excess carriers generated by pulse light illumination and subsequent carrier emission processes from trap states are observed as transient currents. PTPS can be applied to undoped *a*-Si:H, and the energy distribution of electron trap states above the midgap and that of hole trap states below the midgap in *a*-Si:H can be determined by this method when the sample structures and experimental conditions are properly selected, as discussed in our previous publications.[12,13] Therefore, this method is suited to the present purposes. We prepare undoped *a*-Si:H samples in an ultrahigh-vacuum plasma-enhanced chemical-vapor-deposition (UHV-PECVD) chamber and intentionally introduce oxygen atoms by adding CO_2 to the source gases. By comparing the results obtained for high-purity samples and oxygen-doped samples, we will discuss the effects of oxygen on $g(E)$ of undoped a-Si:H in an as-grown state. We will also describe the difference in the light-induced changes in $g(E)$ between high-purity and oxygen-doped samples. It has been found that the presence of oxygen atoms could enhance the defect reactions during the prolonged illumination, while $g(E)$ in the as-deposited state was similar for the high-purity and oxygen-doped samples in the energy range investigated. A light-induced decrease in the density of hole traps has been found and discussed.

II. SAMPLES AND EXPERIMENTS

A. Sample preparation

Undoped a-Si:H films with thicknesses of 1.4–1.5 μm were deposited by plasma-enhanced chemical vapor deposition (PECVD) on n^+ or p^+ Czochralski (Cz) crystalline silicon (c-Si) substrates. This film thickness, 1.4–1.5 μm, was selected to enable the observation of light-induced changes in a-Si:H bulk. The following two points were taken into account in this selection: (1) light-induced changes in undoped a-Si:H can depend on the sample film thickness up to 1 μm and become independent above this value, as observed by Stutzmann *et al.*,[14] and (2) uniform light-induced generation of bulk defects can become difficult for the film thickness over 2 μm since we irradiate the samples with filtered white light, as will be shown later. Resistivities of n^+ and p^+ Si substrates were 0.05–0.1 Ω cm. The PECVD system was the capacitive-coupling type operating at 13.56 MHz. The system was specially designed for the deposition under ultrahigh-vacuum conditions. The background pressure in the deposition chamber was 3.8×10^{-10} Torr. The details of the deposition system have been described elsewhere.[9] The substrate temperature during the deposition was 200 °C. The source gases were silane (SiH_4) and hydrogen (H_2) for ultrapure a-Si:H films, and the flow rates of SiH_4 and H_2 were 10 and 20 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. CO_2 diluted to 1% by H_2 was added to the gas mixture to introduce oxygen into a-Si:H. In the deposition of oxygen-doped a-Si:H, the flow rates of SiH_4, H_2, and CO_2 (diluted by H_2) were 10, 15, and 5 SCCM, respectively. The total pressure, the rf power, and the film deposition rate were 0.05–0.055 Torr, 5 W, and 2.0–2.2 A/s, respectively.

Schottky barrier diodes were fabricated by depositing transparent gate dots on the front surface of a-Si:H films. The diameter of the circular dot was 2 mm, and the dot area was 3.14×10^{-2} cm^2. A double-layer structure of indium tin oxide (ITO) and silicon oxide (SiO_x) was prepared by electron beam (EB) evaporation at 180 °C as the transparent gate on the sample films deposited on n^+ c-Si substrates. The evaporation source for ITO was a mixture of indium oxide (95%) and tin oxide (5%), and that for SiO_x was quartz glass. Oxygen gas was introduced into the evaporation chamber during the preparation of ITO and the chamber pressure was 1.8×10^{-4} Torr. Here, the thickness of the ITO layer and that of the SiO_x layer were 90 and 5 nm, respectively. Since the SiO_x layers were prepared at a low temperature by EB evaporation, the oxygen component x might be less than 2, though detailed studies have not been carried out. An ITO single-layer structure was employed as the transparent gate on the sample films on p^+ c-Si substrates. The thickness and preparation conditions of the ITO layer were the same as those for the double-layer structure described above. An Ohmic contact to the back of the substrates was made by aluminum evaporation at room temperature.

As discussed in Ref. 12, in PTPS measurements, the trap states, located at shallower energy positions and filled with carriers generated by pulse light, emit the trapped carriers in a shorter time and become empty. However, when the leakage currents are high, these empty states can retrap the carriers due to junction leakage and subsequently re-emit these carriers. Therefore, the PTPS signal could become apparently large in a longer time range and, consequently, the density of gap states obtained from the PTPS data would also be apparently higher in a deeper energy range. Therefore, the reduction of leakage currents is essential to exactly determine the energy distribution of gap states by PTPS.

The leakage currents became low and their effects on the PTPS measurements were significantly reduced when the ITO/SiO_x double-layer structure and the ITO single-layer structure were employed as transparent gates in the diodes fabricated on n^+ and p^+ c-Si substrates, respectively. The results of PTPS measurements were not affected by the presence of the SiO_x layers, as discussed in Ref. 13.

B. Experiments

Impurity (O, C, N) concentration in the sample films was measured by secondary ion mass spectrometry (SIMS). The measurement was performed using a PHI ADEPT-1010 system. The primary ion was cesium (Cs^+) and its acceleration voltage was 5.0 kV.

In PTPS measurements, a dye laser (Photon Technology International Inc., model GL301) pumped by a nitrogen laser (Laser Photonics Inc., LN-1000) operating at a wavelength of 460 nm was employed to generate light pulses with a width of 0.6 ns and an energy of 200 μJ/pulse. The intensity of the pulsed light was varied by inserting neutral density filters in front of the samples. A reverse bias voltage pulse from −1 to −8 V was applied to the sample diode 20 μs prior to the light pulse illumination of the sample. Transient photocurrent signals were analyzed using a digitizing signal analyzer (Tektronicx, model DSA 601). A wide-band preamplifier (NF Corp., model BX-31A) and a current amplifier (Stanford Research Systems, model SR570) were used to magnify the signal for the time range between 100 ns and 100 μs and for the time range longer than 30 μs, respectively. The advantages of the SR570 current amplifier in PTPS measurements have been described elsewhere.[12] The signal-to-noise ratio was improved by signal averaging up to 1024 pulses. PTPS signals measured in different time and current ranges were combined into one set of data. The measurement system covers the time range between 10^{-8} and 1 s and the current range from 10^{-13} to 10^{-1} A. The measurement control and data analysis were performed using a personal computer. PTPS measurements were carried out at 297, 325, and 355 K.

The sensitivity and reproducibility of the present PTPS measurements were enough to detect the 20% difference in the density-of-states (DOS) distribution. A typical spread of the results obtained for the several samples prepared under identical conditions was 20%–30%. The difference in the DOS distribution over 30% will thus be discussed when we compare (1) the pure and oxygen-doped samples and (2) the states before and after the prolonged illumination.

Prolonged illumination of samples was performed at room temperature and under filtered white light from a tungsten lamp with an intensity of 470 $\mathrm{mW/cm^2}$. The filter inserted in the light path passed light with wavelengths longer than 610 nm. The illumination time was 3 h and the samples were under the open-circuit condition during the illumination. Although 3 h of illumination was not long enough to observe the saturation of light-induced changes, the observation of initial large changes in the energy distribution of gap states was possible under this condition.

III. PROCEDURE AND ASSUMPTIONS FOR DETERMINING THE ENERGY DISTRIBUTION OF GAP STATES FROM POST-TRANSIT PHOTOCURRENT SPECTROSCOPY DATA

In this paper, we assume[11,12] that the energy distribution of gap states, $g(E)$, is proportional to the product of the observation time t and the transient current (PTPS signal) $I(t)$,

$$g(E) = KI(t)t. \tag{1}$$

Here, K is a prefactor. It is also assumed[10–13] that the trap energy position, E, is given by

$$E = kT\ln(\nu t). \tag{2}$$

Here, k is the Boltzmann factor, T is the absolute temperature of the sample, and ν is the attempt-to-escape frequency. For simplicity, the value of ν is assumed to be $10^{12}\ \mathrm{s^{-1}}$ and independent of energy E in this paper, referring to the literature.[10,11,15]

The product of the observed transient currents $I(t)$ and the time t in Eq. (1) comes from the emission of carriers from traps, as discussed in Refs. 11 and 16–18. On the other hand, the prefactor K in Eq. (1) reflects the trap filling processes which depends on the details of the carrier generation by the pulse light and the subsequent carrier transport in the shorter time range of the measurements. The intensity of the pulse light, F, was selected to be high enough to completely fill the traps by photogenerated carriers in the present experiments.[12] Under this experimental condition, the carrier generation by the pulse light and the subsequent carrier transport became in (electron case) or close to (hole case) the space-charge limited-current (SCLC) regime.[12] Since there is no general theory of PTPS which includes the SCLC case, we do not have an exact formula for K at the present. However, we experimentally confirmed that the PTPS signal saturates for a high intensity F of incident light, as stated above, and also for a high reverse bias voltage V applied to the sample during the measurements in all the samples studied. These results imply that the trap filling was satisfactory in the present experiments though the functional form of K, $K = f(F,V)$, is not clearly given at the present. Equation (1) has been, therefore, justified as a relative measure of $g(E)$ in the present experiments and can be utilized for the comparison between high-purity and oxygen-doped samples and for the analysis of light-induced changes.

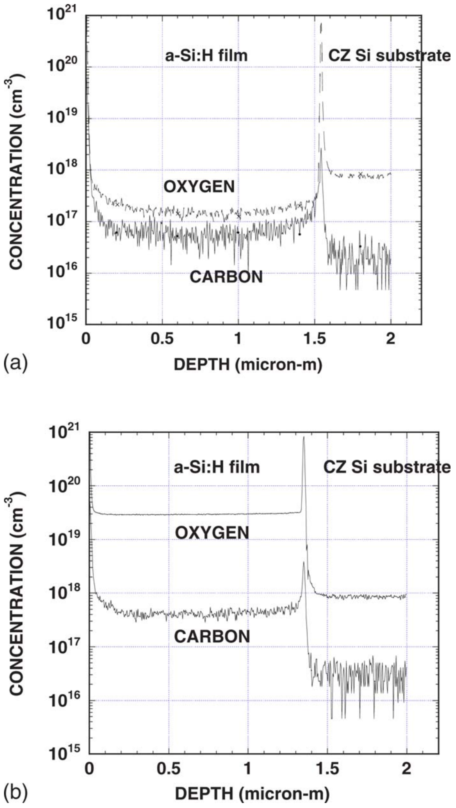

FIG. 1. (Color online) Depth profile of oxygen and carbon atoms in (a) high-purity sample and (b) oxygen-doped sample. The detection limit of the SIMS measurement was 2×10^{17} and $1.5\times10^{16}\ \mathrm{cm^{-3}}$ for oxygen and carbon atoms, respectively.

As for the value of the attempt-to-escape frequency ν for hole traps, we have experimentally confirmed that ν is indeed constant ($10^{12}\ \mathrm{s^{-1}}$) and irrespective of energy in both high-purity and oxygen-doped samples and that ν remains unchanged before and after the long exposure to light. The details will be described in Sec. IV. On the other hand, concerning the value of ν for electron traps, large leakage currents impeded the PTPS measurements at higher temperatures, which are necessary for such confirmation, as will be shown also in Sec. IV. Therefore, we must mention that the constant ν is a first-order approximation in the electron case.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Impurity concentration in high-purity and oxygen-doped *a*-Si:H films

Figure 1 displays depth profiles of oxygen and carbon in (a) an *a*-Si:H film without intentional impurity doping and (b) an oxygen-doped *a*-Si:H film, both of which were deposited on Cz Si substrates. In the former sample, oxygen con-

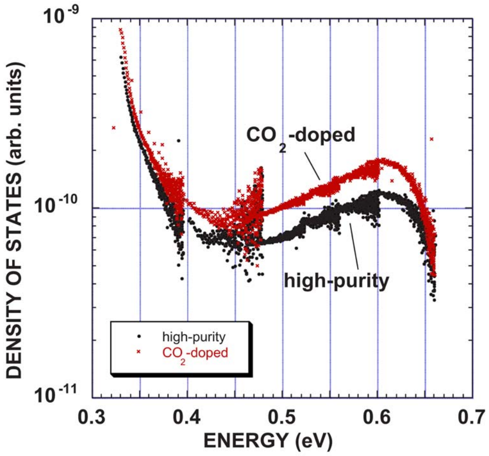

FIG. 2. (Color online) Energy distribution of electron trap states in high-purity sample and in oxygen-doped sample. The PTPS measurements were performed at 297 K. The samples were in an as-deposited state.

tent was comparable to or lower than the detection limit of the SIMS measurement (2×10^{17} cm^{-3}). The depth profile of carbon was fairly uniform in the bulk of this sample and its concentration was 6×10^{16} cm^{-3}, which is higher than the background level (1.5×10^{16} cm^{-3}). The concentration of oxygen and that of carbon atoms in this sample are much lower than those in ordinary device-grade *a*-Si:H films,[1] and we assume that the film properties are unaffected by the presence of these impurities. We thus refer to this sample as the high-purity sample in this paper. CO_2 doping increased the concentrations of oxygen and carbon to 3×10^{19} and 4×10^{17} cm^{-3}, respectively. The depth profiles of these impurities were almost uniform, as shown in Fig. 1(b). The carbon concentration of 4×10^{17} cm^{-3} is still low enough to have negligible effects on the properties of *a*-Si:H.[2] On the other hand, the oxygen content of 3×10^{19} cm^{-3} is typical of that found in device-grade *a*-Si:H,[1] and significant changes in the film properties are expected to occur because of the presence of oxygen atoms at this concentration.[2,3] Therefore, we refer to this sample as the oxygen-doped sample in this paper. The concentration of hydrogen was 5×10^{21} cm^{-3}, and there was no difference between the high-purity sample and the oxygen-doped sample. In both samples, the nitrogen content was lower than the detection limit of the SIMS measurement (1×10^{16} cm^{-3}).

B. Effects of oxygen impurity on energy distribution of gap states in as-deposited *a*-Si:H

Figure 2 shows the energy distribution of electron trap states determined from PTPS data measured at 297 K for the high-purity and the oxygen-doped samples. The procedure to obtain the energy distribution of trap states from PTPS data was described in Sec. II. Both samples were in an as-deposited (virgin) state. The energy on the horizontal axis was measured from the conduction-band edge. It has been found for both the high-purity and the oxygen-doped samples that (1) a conduction-band tail extends up to 0.40 eV from the conduction-band edge, (2) the energy distribution of gap states gradually increases, and (3) a broad peak is observed at around 0.60 eV. A similar energy distribution can be found in the literature.[10,15,19] The broad peak located at around 0.60 eV can be ascribed[15,19] to a negatively charged Si dangling bond, $D(-/0)$. The density of the $D(-/0)$ state is 60% higher in the oxygen-doped sample. Since the leakage currents are low at 297 K in these samples, no apparent increase in the density of gap states in a deeper energy range[12] is observed. As stated in the introduction, it has been reported[2–4] that oxygen can form a donorlike state in the upper gap of undoped *a*-Si:H. However, no specific feature in $g(E)$ is found in the oxygen-doped sample in the energy range investigated (0.35–0.65 eV). In PTPS measurements on these samples, the effects of carrier transit, instead of carrier emission from trap states, are predominant in the time range shorter than 700 ns, which corresponds to the energy depth of 0.35 eV in Fig. 2. Therefore, PTPS measurements do not yield $g(E)$ for the energy range shallower than 0.35 eV. The results in Fig. 2 imply that the donorlike states related to oxygen, if any, are located at the energy position shallower than 0.35 eV from the conduction-band edge.

Figure 3 displays the energy distribution of hole trap states of (a) the high-purity and (b) the oxygen-doped samples, both of which were in the as-deposited state. The energy on the horizontal axis was measured from the valence-band edge. $g(E)$ determined from the data measured at 297, 325, and 355 K is presented for each sample in this figure. We can see a good overlap of $g(E)$ data obtained at these three temperatures in both samples. As mentioned in Sec. III, we assumed, in this analysis, that the attempt-to-escape frequency ν is 10^{12} s^{-1} and independent of energy. If these assumptions were invalid, we would not observe the overlap of the three $g(E)$ curves obtained at different temperatures. Therefore, the results in Fig. 3 confirm the validity of the assumptions on ν. Unfortunately, in the case of electron traps (Fig. 2), a similar test of the validity was not possible since accurate measurements became difficult at 325 and 355 K because of high leakage currents at these temperatures. In both samples, a broad valence-band tail state extends up to 0.45 eV from the top of the valence-band edge and then the gap state density increases with energy. The results in the energy range between 0.40 and 0.46 eV are rather noisy since the sensitivity of the broad-band preamplifier employed to measure this part was insufficient to realize a high signal-to-noise ratio. Balberg *et al.*[5] suggested that acceptorlike states, possibly induced by the presence of oxygen, may lie 0.3–0.5 eV above the valence-band edge, on the basis of their experimental results on the sensitization of electron lifetime in *a*-Si:H. The oxygen content in the present oxygen-doped sample is 3×10^{19} cm^{-3}, which is 1 order of magnitude higher than that assumed in the analysis of Balberg *et al.*[5] However, we do not find any meaningful difference in $g(E)$ in the energy range studied (0.38–0.50 eV)) between the high-purity sample and the oxygen-doped sample, as shown in Fig. 3. We thus argue that oxygen-induced states do not exist in this energy range in the present sample.

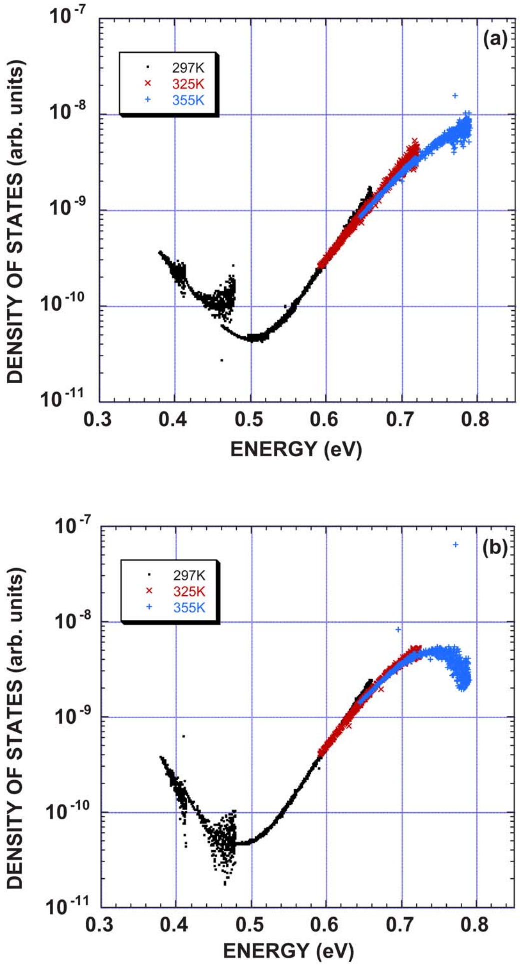

FIG. 3. (Color online) Energy distribution of hole trap states in (a) high-purity sample and (b) oxygen-doped sample. The PTPS measurements were performed at 297, 325, and 355 K. Dots (·), saltire crosses (×), and crosses (+) represent the results obtained at 297, 325, and 355 K, respectively. The samples were in an as-deposited state.

For the energy range deeper than 0.5 eV, the density of hole traps increases with energy in both the high-purity and oxygen-doped samples, as shown in Fig. 3. The energy distribution of hole traps is similar between the two samples. However, some difference is seen; a peak at 0.74 eV is observed in the oxygen-doped sample while no clear peak is seen in the high-purity sample for the energy range investigated. One possible origin of the peak observed at 0.74 eV would be a neutral Si dangling bond, $D(0/+)$.[20] However, we rule out this explanation on the basis of the experimental results on the light-induced changes of these hole trap states, which will be described and discussed in Sec. IV C.

C. Light-induced changes in energy distribution of gap states in high-purity and oxygen-doped *a*-Si:H

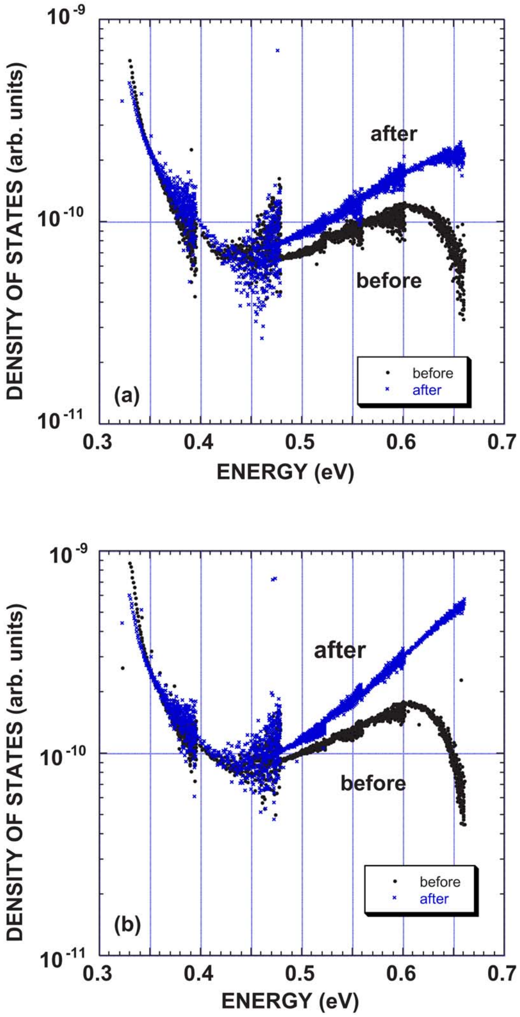

FIG. 4. (Color online) Energy distribution of electron trap states before and after long exposure to light in (a) high-purity sample and (b) oxygen-doped sample. The PTPS measurements were performed at 297 K. The prolonged illumination of samples was performed at room temperature and under filtered white light from a tungsten lamp with an intensity of 470 mW/cm^2. The illumination time was 3 h and the samples were under the open-circuit condition during the illumination.

Figure 4 shows the light-induced changes in the energy distribution of electron trap states of (a) the high-purity sample and (b) the oxygen-doped sample. The prolonged illumination increased the density of electron traps in the energy range between 0.4 and 0.65 eV in both samples, which can be ascribed to the light-induced generation of Si dangling bonds. On the other hand, the broadening of the conduction-band tail upon long exposure to light[15] was not observed in these samples. Although no clear peak in $g(E)$ was seen after light soaking in the energy range studied, the results in Fig. 4 indicate that light-induced Si dangling-bond states are located at deeper energy positions than the states present in as-grown samples. A similar observation has been reported by Yan *et al.*[11] The surroundings of the light-induced Si dangling bonds might be different from those of the Si dangling bonds present in as-deposited films. Another possible explanation is that the attempt-to-escape frequency ν increased upon long exposure to light; the increase in ν results in the shift of the trap energy to the deeper side [see

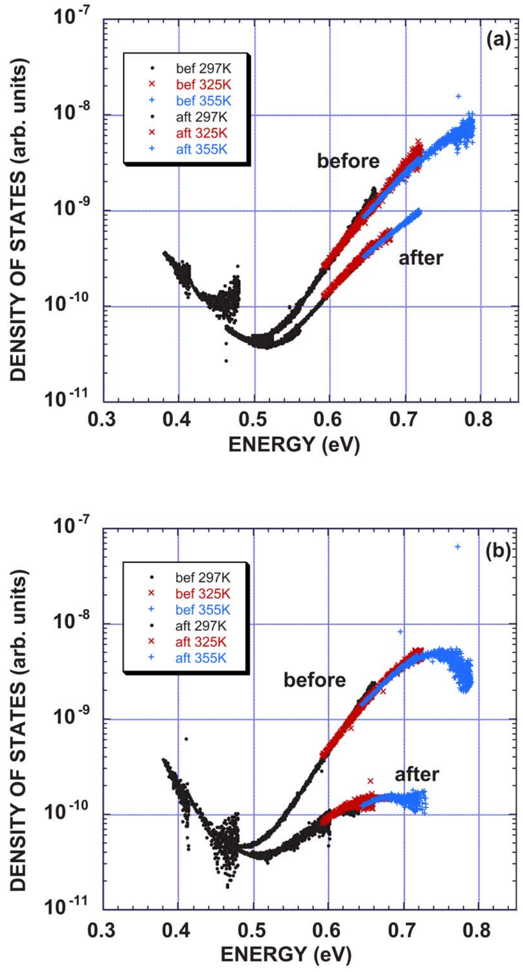

FIG. 5. (Color online) Energy distribution of hole trap states before and after the long exposure to light in (a) high-purity sample and (b) oxygen-doped sample. The PTPS measurements were performed at 297, 325, and 355 K. Dots (·), saltire crosses (×), and crosses (+) in the figure represent the results obtained at 297, 325, and 355 K, respectively. The prolonged illumination of samples was performed at room temperature and under filtered white light from a tungsten lamp with an intensity of 470 mW/cm^2. The illumination time was 3 h and the samples were under the open-circuit condition during the illumination.

Eq. (2)]. It is, however, difficult to judge whether this explanation is valid since the value of ν for electron traps cannot be experimentally determined in the present samples, as described in Sec. IV B. The light-induced changes in the energy distribution of electron traps were larger in the oxygen-doped sample. We thus argue that the presence of oxygen at a concentration of 3×10^{19} cm^{-3} in *a*-Si:H enhances the light-induced changes. As observed and discussed by Kamei *et al.*,[9] there would be no one-to-one correlation between light-induced defects and oxygen atoms. However, oxygen atoms could affect the defect reactions that take place during prolonged illumination.

Figure 5 shows the light-induced changes in the energy distribution of hole trap states of (a) the high-purity sample and (b) the oxygen-doped sample. $g(E)$ results determined from the data measured at 297, 325, and 355 K are displayed for each sample in this figure. Also, in the light-soaked state, we see a good overlap of $g(E)$ curves obtained at these three temperatures in both samples. Therefore, the assumptions on ν, discussed in Sec. III, are valid after the prolonged illumination. Upon long exposure to light, little change is observed in $g(E)$ for the energy range shallower than 0.45 eV (deep valence-band tail region). Stutzmann[21] argued that deep valence-band tail states can originate from Si weak bonds and that the density of these states may decrease upon long exposure to light, since the Si weak bonds could be converted into Si dangling bonds during prolonged illumination. However, we do not observe the change in the energy distribution of deep valence-band tail states in the present samples. On the other hand, the density of hole traps is significantly reduced by the prolonged illumination for the energy range deeper than 0.45 eV in both samples. The decrease in the hole trap density is larger in the oxygen-doped sample. Since the PTPS signal becomes smaller after light soaking, reflecting the decrease in the defect density, it is difficult to determine $g(E)$ exactly for the energy range deeper than 0.72 eV in the light-soaked samples. Therefore, $g(E)$ curves are not shown for this energy range in Fig. 5.

Hata and Matsuda[22] observed the light-induced annealing of deposition-induced defects in undoped *a*-Si:H. However, they did not report the energy distribution of defect states or the changes in hole trap states. Light-induced annealing of deep hole traps was not discussed nor predicted in the theories[23,24] of the energy distribution of defect states in *a*-Si:H. In contrast with the present results, Kocka *et al.*[16] observed the light-induced increase in the density of hole trap states in the energy range between 0.4 and 0.6 eV, also by PTPS measurements. The sample structure used by Kocka *et al.* was glass/TCO/*n*-*i*-*p* *a*-Si:H layers, and the film thickness of the undoped (*i*) layer was 0.43 μm. We also observed,[12,13] by PTPS, the light-induced increase in the deep hole trap density when the sample thickness was 0.6 μm. Here, the samples in our previous report were prepared in the deposition system other than that utilized in the present study. While Stutzmann *et al.*[14] observed the thickness dependence of the density of light-induced Si dangling bonds, the present results, those from Kocka *et al.*, and those in our previous publication indicate that the light-induced changes in the deep hole traps are also dependent on the film thickness.

We can discuss the origin of the hole trap states observed in the energy range deeper than 0.5 eV referring to the data in Figs. 3 and 5. If the origin of these hole trap states were a neutral Si dangling bond, $D(0/+)$, we would observe an increase in their density upon long exposure to light that corresponds to the observed increase in the density of negatively charged Si dangling bonds, $D(-/0)$, shown in Fig. 4. This is not the case, as shown in Fig. 5. We can thus say that these hole trap states should have an origin other than $D(0/+)$. Si dangling bonds coupled with oxygen atoms could be another possible origin for the hole trap states. However, the energy distributions of these states are similar in the high-purity and oxygen-doped samples, as shown in Fig. 3, despite a more than 2 orders of magnitude difference in the oxygen content. Moreover, the density of states at 0.78 eV in the high-purity

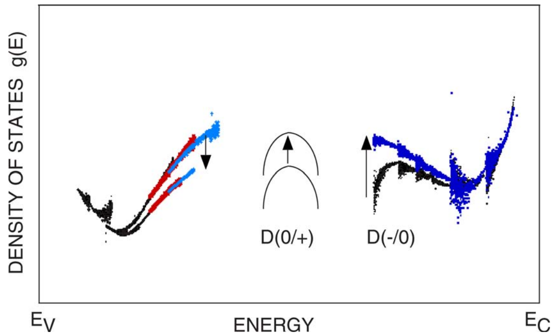

FIG. 6. (Color online) Schematic energy distribution of gap states and light-induced changes (denoted by arrows) in *a*-Si:H based on the experimental results obtained in this study. Horizontal and vertical axes are not to scale. E_c and E_v denote the conduction-band edge and the valence-band edge, respectively. A neutral Si dangling-bond state, $D(0/+)$, is shown, although information regarding this state was not obtained in the present experiments.

sample is somewhat higher than the peak density at 0.74 eV of the oxygen-doped sample, although a clear peak is not observed in the former sample. Therefore, it is difficult to ascribe the origin of the hole trap states located in the energy range deeper than 0.45 eV to the Si dangling bonds coupled with oxygen atoms. These results are in contrast with the case of Si dangling bonds coupled with phosphorus atoms ($^{-}D^{*}$ states) reported by Okushi[25] where the density of $^{-}D^{*}$ states increases with phosphorus concentration. Further study is required to clarify the origin of the deep hole trap states. As discussed in the previous paragraph, the light-induced changes in the deep hole traps depend on the film thickness. This dependence should be taken into account in the further discussion of the origin of the deep hole traps.

Both the light-induced increase in $D(-/0)$ states (Fig. 4) and the light-induced decrease in the hole trap states (Fig. 5) were observed in the high-purity and the oxygen-doped samples, as schematically shown in Fig. 6. These experimental results might suggest that defect conversion processes are taking place during the long exposure to light; Si dangling bonds were generated from the precursors or latent sites which manifested as hole trap states located between 0.5 and 0.75 eV in $g(E)$. However, the energy range of the present PTPS measurements was not wide enough to draw a clear conclusion on the light-induced changes. In the deeper energy side, the effect of leakage currents still limits the measurements. For example, we did not observe the exact shape of $g(E)$ for the electron traps after light soaking, as displayed in Fig. 4. Regarding the hole traps, the energy range covered was not enough to determine the whole shape of $g(E)$ before and after the prolonged illumination, as shown in Fig. 5. Since the present PTPS system covers the time range up to 1 s, the measurements at 355 K will allow us to observe the trap states located at 0.85 eV from the relevant band edge. Here, we assume again that the value of ν is $10^{12}\ \mathrm{s}^{-1}$. There is thus much room for the expansion of the measurements toward a deeper energy range when the leakage currents are further reduced. For the shallower energy range, the carrier transit limits the measurements, as discussed in Sec. IV B. Since this is a fundamental limit of PTPS, a combination of other experimental methods would be necessary to observe the energy distribution of gap states in the shallower range. If the energy range of $g(E)$ measurements is expanded, we may observe other aspects of the light-induced changes more clearly.

V. CONCLUSIONS

In this work, we have studied the effects of oxygen impurities on the energy distribution of gap states, $g(E)$, in undoped *a*-Si:H. We prepared undoped *a*-Si:H samples in an UHV-PECVD chamber and intentionally introduced oxygen atoms by adding CO_2 to the source gases. The oxygen content in the high-purity sample was comparable to or lower than the detection limit of the SIMS measurement ($2\times10^{17}\ \mathrm{cm}^{-3}$), while CO_2 doping increased the concentration of oxygen to $3\times10^{19}\ \mathrm{cm}^{-3}$. PTPS was employed to obtain $g(E)$. This experimental technique was beneficial particularly for observing the energy distribution of hole traps. We obtained the following results.

(1) No specific feature was found in the energy distribution of electron trap states of the oxygen-doped sample in the energy range investigated (0.35–0.65 eV). This result implies that the donorlike states related to oxygen, if any, are located at energy positions shallower than 0.35 eV from the conduction-band edge.

(2) We did not find any meaningful difference in the energy distribution of hole trap states in the energy range of 0.38–0.50 eV from the valence-band edge when we compared the high-purity sample and the oxygen-doped sample. We thus argued that oxygen-induced states, as suggested by Balberg *et al.*, do not exist in this energy range in the present sample.

(3) Si dangling-bond defects were generated by prolonged illumination in both the high-purity and oxygen-doped samples. The light-induced increase in the density of Si dangling-bond states was larger in the oxygen-doped sample.

(4) Upon long exposure to light, little change was observed in the energy distribution of hole trap states for the energy range shallower than 0.45 eV (deep valence-band tail region) in both the high-purity and oxygen-doped samples. On the other hand, the density of hole traps was significantly reduced by the prolonged illumination for the energy range deeper than 0.5 eV in both samples. The decrease in the hole trap density was larger in the oxygen-doped sample.

(5) The hole trap states observed in the energy range deeper than 0.5 eV cannot be ascribed to neutral Si dangling bonds, $D(0/+)$, since the light-induced decrease in the density of these hole trap states does not coincide with the light-induced increase in the density of negatively charged Si dangling bonds, $D(-/0)$. We rule out another hypothesis that a Si dangling bond coupled with an oxygen atom may be an origin of the hole trap states since the energy distributions of these states were similar in the high-purity and oxygen-doped samples despite a more than 2 orders of magnitude difference in the oxygen content.

Although we have obtained some experimental results, that is, the presence of deep hole traps that exhibit light-induced annealing and the enhancement of defect reactions during the prolonged illumination because of the presence of oxygen, the details remain unexplained and more in-depth investigation is necessary to understand the underlying mechanisms. Further reduction of the leakage currents of diode samples and combinations with other experimental methods are required in the next stage of studies.

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