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## Measurement of the Surface Recombination Velocity S at the Si-SiO<sub>2</sub> Interface by the Dual-Mercury Probe Method

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A novel measurement technique of the surface recombination velocity S at the  $Si-SiO_2$  interface by the dual-mercury probe method is proposed. It is shown that the S experimentally obtained has the pyramid-like peak from near flatband to midgap condition and takes an extremely low value less than 10 cm/s at both inversion and accumulation condition. In addition, the S is compared with the interface-state density  $D_{1\pm}$ .

#### 1. Introduction

The thermally grown Si-SiO<sub>2</sub> interface is the essential material system for many Si devices. Numerous characterization techniques for the interface are generally concerned with the measurement of the majoritycarrier properties<sup>1)</sup>. For minority-carrier devices such as a solar cell, it is important, however, to understand the properties of minority carriers, e.g., electron-hole recombination at the interface. The recombination is usually characterized by a surface recombination velocity S, that corresponds to a minority-carrier lifetime  $\tau$  in the Si bulk. The S expressed by the Shockley-Read-Hall (SRH) statistic is a complex function of Si-SiO<sub>2</sub> interface properties, i.e., the density and capture cross section of Si-SiO<sub>2</sub> interface states, and surface carrier densities<sup>2)</sup>. Therefore, a technique to experimentally determine the S must be required. To our knowledges, very few works have been reported so  $far^{3}$ .

In this paper, a novel measurement technique of the S at the  $Si-SiO_2$  interface based on the dual-mercury probe method<sup>5),6)</sup> is described. It is shown that the S at different Si-SiO<sub>2</sub> interfaces is successfully evaluated as a function of a gate bias voltage. The experimental results are investigated, comparing with the interface-state density  $D_{\pm t}$ .

# Experimental and analytical method Measurement setup and samples

The measurement setup for the evaluation of S is schematically shown in Fig.1. Two mercury probes (0.5mm $\phi$ ,space:5mm) made contacts with the HF-etched back surface of the oxidized Si wafer sample through a Mylar orifice plate by vacuum-pumping through a little gap between the Mylar plate and the wafer.

The measured samples were n-type, (100)oriented,  $17-22 \Omega$ -cm, FZ Si wafers, oxidized in dry  $0_2$  (Si $0_2 \sim 800A$ ) and followed by evaporation of Indium Tin Oxide (ITO) films as transparent gates. One sample was annealed in  $0_2$  at 800°C for 30min before the ITO evaporation. Another sample was annealed in H<sub>2</sub> at 400°C for 30min after the dry  $0_2$ oxidation and ITO evaporation to reduce the



Fig.1 Schematic measurement setup for the dual-mercury probe method for the evaluation of the surface recombination velocity S at the Si-SiO $_{2}$  interface.

Si-SiO<sub>2</sub> interface-state density.

The intensity-modulated light (GaAs LED: 3mW) illuminated the ITO gate to generate minority carriers near the Si-SiO2 interface. One Hg probe situated beneath the ITO gate was reversely biased to collect a part of photo-generated minority carriers diffused from the vicinity of the Si-SiO<sub>2</sub> interface. A gate voltage was applied to change surface The DC bias light of a W-lamp band vending. (50 mW/cm<sup>2</sup>) also illuminated the whole front surface of the sample to reduce the resistance of the measurement circuit. The frequency-dependent photocurrent was measured as a function of gate bias voltage by using a 100kHz lock-in amplifier. To determine the au and D of the sample, the similar measurement of the photocurrent was also performed The interfaceat the sandblasted surface. state density Dit of each sample was estimated by the quasi-static and highfrequency C-V measurement.

2.2 Evaluation procedures of the surface recombination velocity S

The evaluation of the  $\tau$  and D of minority carriers in the Si wafer using the dual-mercury probe method has been presented previously in detail<sup>5</sup> and will therefore only be reviewed here. The behavior of the photo-generated minority carriers is ap-

proximately dealt with to be one-dimensional for brevity. Because the applied DC bias appears mainly in the depletion region of the reversely biased Hg contact. In such a case, the photocurrent picked up by the Hg contact is expressed as a solution of continuity and diffusion equations with adequate boundary conditions7) and is a complicated function with three unknown parameters,  $\tau$ , D, and S. One way to simplify the analytical solution is to eliminate one of these parameters. It has been shown that, for S higher than around 10<sup>6</sup> cm/s, the normalized photocurrent is independent on the value of S<sup>5</sup>). We adopt this limited case for the evaluation of  $\tau$  and D by measuring the sandblasted surface of the wafer sample. For the case of W/L>3 and  $\omega \tau$  » where  $L = \sqrt{\tau D}$  and  $\omega$  is an angular 1. frequency,  $\tau$  and D have been shown to be able to be graphically determined from the simplified analytical formula<sup>5)</sup>. However. even for the other cases, we can obtain auand D by curve-fitting with the aid of calculated correction factors. After the determination of  $\tau$  and D, the dependence of the photocurrent on S can be calculated as a function of modulation frequency. Then the S at given surface on the wafer sample can be evaluated by comparing the experimental data with the corresponding calculations. In other words, the proposed technique makes it possible to determine  $\tau$  and S separately. The accuracy of the determined S is generally improved for a wafer sample with longer minority-carrier lifetime and/or larger thickness. The above-mentioned procedures were used for the evaluation of the S at the Si-SiO<sub>2</sub> interfaces as a function of the gate bias voltage.

The energy distribution of the Si-SiO<sub>2</sub> interface-state density  $D_{1\pm}$  was measured by a conventional quasi-static and high-frequency C-V method to compare it with the experimentally obtained S.



Fig. 2 Dependence of the surface recombination velocity S on gate bias voltage at the Si-SiO<sub>2</sub> interface annealed in O<sub>2</sub> at 800°C for 30min after the dry O<sub>2</sub> oxidation. The gates were transparent ITO films.

### 3. Experimental results and discussions

Figure 2 shows the experimental results of the log(normalized photocurrent) vs. square root of frequency  $(\sqrt{f})$  characteristics for the Si-SiO<sub>2</sub> sample annealed in O<sub>2</sub>. For the calculation shown by solid curves in Fig. 2, the experimentally evaluated  $\tau$  of 150  $\mu$  s, D of 11.3cm²/s, and W of 522  $\mu$  m were used. The dependence of the surface recombination velocity S on gate bias voltage was then determined and is plotted in Fig.3 for both samples. For the O2-annealed sample, it is obvious from Figs. 2 and 3 that the S of photo-generated minority carriers is less effective under both accumulation and inversion conditions due to lack of either majority or minority carriers at the Si-SiO<sub>2</sub> interface, which is in good agreement with the theoretical works<sup>3),4),8)</sup>. This experimental



Fig. 3 Dependence of the surface recombination velocity S on gate bias voltage at the Si-SiO<sub>2</sub> interface annealed in O<sub>2</sub> at 800°C for 30 min after the dry O<sub>2</sub> oxidation ( $\bigcirc$ ), and the Si-SiO<sub>2</sub> interface annealed in H<sub>2</sub> at 400°C for 30 min after the dry O<sub>2</sub> oxidation and the ITO evaporation ( $\bigcirc$ ). The limit of the determination of S is about 1 cm/s.

result means that strong band bending at the semiconductor surface is quite effective to reduce the carrier recombination whether high Dit exists or not, and is suggestive for realization of a high efficiency solar cell. The broad peak of S for the sample annealed in  $0_2$  may be due to a high level injection condition. Under moderate band vending or flatband condition, the S depends on  $\mathtt{D}_{\texttt{it}}$  and capture cross sections,  $\sigma_{\mathbf{p}}$  and  $\sigma_{\mathbf{n}}$  of the interface states. The Dit determined by the quasi-static (sweep rate:0.02V/s) and highfrequency (100kHz) C-V measurement are plotted in Fig. 4, which indicates nearly constant and high level value within the measurement for the O<sub>2</sub>-annealed sample. At near midgap region, a high level injection condition of ns=ps》 n1 was fulfilled. In that case, the experimentally obtainable S is



Fig. 4 Interface-state density  $D_{1+}$  as a function of energy for the  $O_2$ -annealed sample ( $\bigcirc$ ), and the H<sub>2</sub>-annealed sample ( $\bigcirc$ ).  $D_{1+}$  was determined by the quasi-static and high frequency C-V measurement.

expressed as  $v_{th} \{\sigma_p \sigma_n / (\sigma_p + \sigma_n)\}$  (integral of Dit with energy), where Vth is the average thermal velocity of carriers. By using this relation and the experimental data for the O<sub>2</sub>-annealed sample in Figs. 3 and 4, the smaller capture cross section is estimated to be 5-7x10-18 cm<sup>2</sup>. It has been reported that  $\sigma_{\mathbf{p}}$  is smaller than  $\sigma_{\mathbf{n}}^{\mathbf{3}}$ . Therefore the obtained capture cross section is considered for holes. However the data for the O<sub>2</sub>-annealed sample in Fig. 3 show the high value of S even near flatband condition, which means whether  $\sigma_{\mathbf{p}}$  still has the order of  $10^{-16}$  cm<sup>2</sup> in upper bandgap and/or  $\sigma_{n}$ takes the order of  $10^{-16}$  cm<sup>2</sup>. It must be said, therefore, that more works for various samples are necessary. For the H2-annealed sample, the peak value of S is suppressed less than 50 cm/s as experimentally shown in Fig. 3. This satisfactorily corresponds to the fact that the Dit indicates 1.5-2 order less than for the O2-annealed sample as shown in Fig. 4. The situation of the quite low S under accumulation and inversion condition is the same as for the sample annealed in  $0_2$ . It is apparent that a well-prepared Si-SiO<sub>2</sub> interface is also effective to reduce the surface carrier recombination.

#### 4. Conclusion

The novel measurement technique of the surface recombination velocity S at the Si-SiO<sub>2</sub> interface based on the dual-mercury probe method has been proposed. The S for the Si-SiO<sub>2</sub> interfaces with different  $D_{1+t}$  has successfully been evaluated as a function of gate bias voltage. For each sample, the quite low S under accumulation and inversion condition and the  $D_{1+t}$ -dependent pyramid-like peak of S from midgap to flatband condition have been observed. The information obtainable by the proposed technique is quite useful for many minority-carrier devices, especially for solar cell design.

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