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Contactless and Nondestructive Characterization of Silicon Surfaces by Capacitance-Voltage and Photoluminescence Methods

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Contactless and nondestructive characterization of the electrical properties of the free surfaces of single crystalline silicon wafers are made for the first time by combined use of the contactless capacitance-voltage(C-V) method and the photoluminescence surface state spectroscopy(PLS^3) technique. The air-exposed and hydrogen-terminated free (111) of silicon surface are shown to be characterized by high surface densities causing Fermi level pinning.

1. Introduction

Quality of surface is supremely important for successful fabrication of silicon ULSI devices and high-efficiency solar cells. Surface trapping states introduced during processing are known to cause very serious effects on device performance. However, there has been no well established suitable method for contactless and nondestructive characterization of the electronic properties of "free" surfaces of silicon wafers before and after processing.

In this paper, the electronic properties of air-exposed and hydrogen-terminated "free" surfaces of single crystalline silicon wafers are successfully characterized in contactless and nondestructive fashion, for the first time, using a contactless capacitance-voltage (C-V) method[1] and the photoluminescence surface state spectroscopy (PLS^3) technique[2].

2. Principle and apparatus of the contactless and nondestructive C-V and PL characterization methods

2.1 Contactless C-V methods[1]

The contactless C-V measurement was made using a commercial measurement system (CV-8000, Dainippon Screen MFG Co. Ltd.). The principle of the contactless C-V method is shown in Fig.1. The Si wafer sample is positioned on the sample stage, being separated from the top electrodes by an "air-gap". The three surrounding parallelism electrodes of the top four electrodes maintain a constant "air-gap" distance of 300 - 350 nm through a piezo-mechanism with capacitance feedback. The C-V characteristics of the MIS system including the contribution from the air-gap insulator are then measured by using the reference electrode which is located in the center.

2.2 Principle of PLS^3 technique

The PLS^3 technique is a novel surface characterization technique intended for determination of the surface state density distribution. In this technique, the band-edge photoluminescence efficiency, defined by the band-edge PL intensity I_{PL}, divided by the excitation intensity, ϕ, i.e., I_{PL}/ϕ, is measured as a function of ϕ, as schematically shown in Fig.2. The PL efficiency changes rapidly in the transition region between high and low excitation regions and this is related to the saturation of surface states for recombination. Since the quasi-Fermi levels for electrons and holes scan the surface band gap in this region, the behavior of the PL efficiency in this region strongly reflects the N_{ss} distribution. Thus, the N_{ss} distribution can be determined by the measured I_{PL}/ϕ with the results of rigorous computer simulation taking account

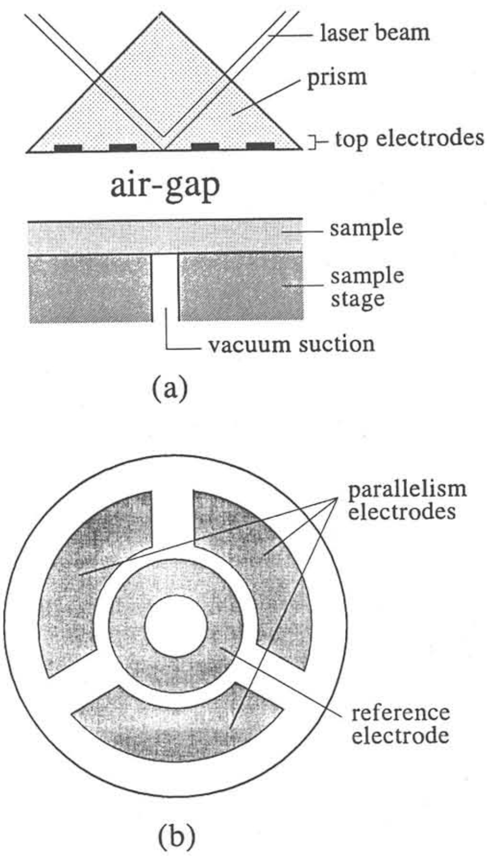

Fig.1 Principle of contactless C-V measurement (a) set-up (b) patterns of top

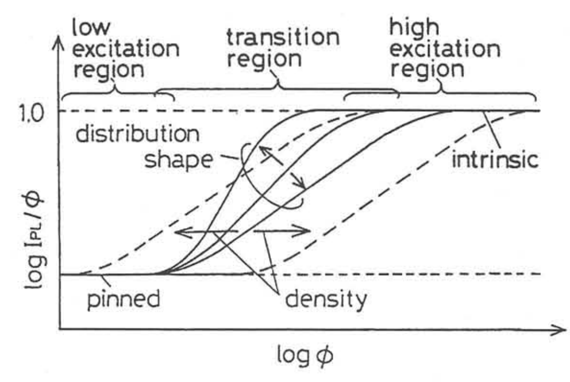

Fig.2 Behavior of PL efficiency used in PLS[3] technique

of all possible recombination processes. Roughly speaking, the slope of the PL efficiency gives the distribution shape, being close to unity for discrete distribution and less steep for continuous distribution. The procedure of the computer analysis were given in detail in the reference 2). For measurement of the PL efficiency spectrum, an automatic PL measurement system which is fully automated by computer control was used. This excitation source was an Ar^+ laser light with a wavelength of 514.5nm.

3. Experimental results and discussions

3.1 Sample preparation

Experiments were done on three kinds of n-type silicon (111) wafers whose surfaces are air-exposed, hydrogen-terminated and thermally oxidized. The thermally oxidized surface was used as a reference. The carrier concentration of wafers was 1-2 x 10^{15} cm^{-3}. Hydrogen termination of the surface was made by the method after Higashi et al.[3] Namely, an about 150nm thick thermal oxide films was formed in dry oxygen at 1000°C. Then, after removing this oxide films in a buffered hydroflouric acid, a native oxide films was formed in an HCl-H_2O_2 solution at 80°C for 10 minutes. Finally, immersion into a 40% NH_4F produced an atomically flat hydrogen-terminated silicon (111) surface.[3),4)] After each process, the sample was rinsed for 10 minutes in the deionized water. The thermally oxidized surfaces were prepared in dry O_2 at 1000°C for 3 hours and annealed for 30 min. in dry N_2.

3.2 C-V measurement

The results of C-V measurements are summarized in Fig. 3. The measurement frequency was fixed at 0.5 MHz. The insulator capacitance, C_I was estimated from the air-gap distance assuming that the relative dielectric constant of the air was equal to 1. As seen Fig.3(a), well behaved C-V curves were obtained on the thermally oxidized surface with the presence of some amount of positive charges are exists. The hysteresis which is seen only in the deep depletion region comes from the nonequilibrium supply of the minority carriers. On the other hand, a very large positive flat-band voltage shift and less steep C-V variation were observed for the air-exposed surface, as seen in Fig.3(b). This indicates the existence of large amount of negative charge at surface as well as a high density of interface states. In the hydrogen-terminated surface shown in Fig.3(c), no such large flat-band voltage shift existed, but strong Fermi level pinning was indicated by an almost flat-band capacitance under positive bias. The N_{ss} distributions determined from the C-V curves are shown in Fig.4. In order further to confirm the difference in the zero-bias Fermi level positions in air-exposed and hydrogen-terminated surfaces, XPS peak shifts of Si 2p core levels were measured. As shown in Fig.5, zero-bias pinning positions agreed fairly well between C-V and XPS methods.

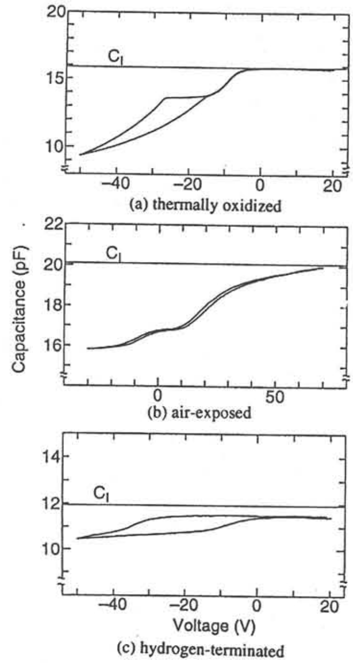

Fig.3 The C-V curves by contactless C-V method

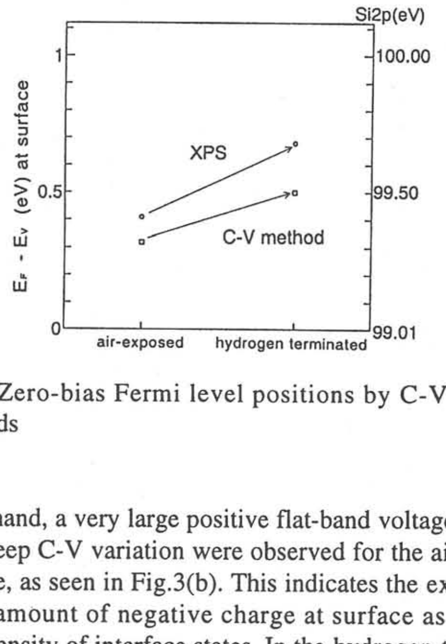

Fig.4 Zero-bias Fermi level positions by C-V and XPS methods

3.3 The PLS[3] measurement

Figure 6 summarizes the results of PL measurements. The PL efficiency of thermally oxidized surface is roughly 10-100 times larger than those of air-

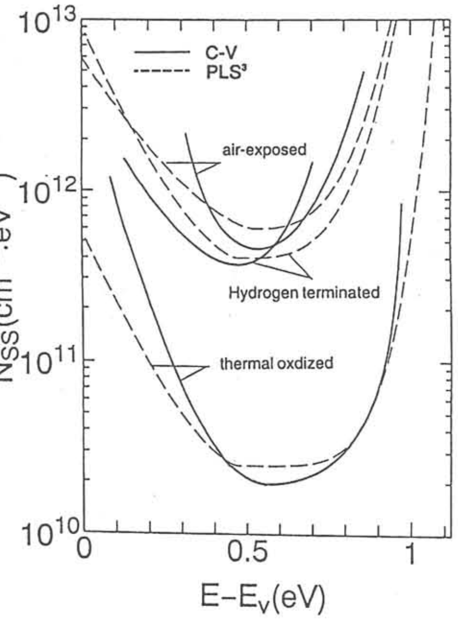

Fig.5 Determined N_{ss} distributions

exposed and hydrogen-terminated surfaces. This indicates that the non-radiative surface recombinations is suppressed by thermal oxidation. The solid curves in Fig.6, are the fitted theoretical curves including the effect of fixed surface charge that is consistent with C-V curves. The N_{ss} distributions which were determined by the PLS^3 method are also shown in Fig.4. Both of the C-V and PLS^3 determination of N_{ss} distribution are in good agreement. Thus, air-exposed and hydrogen-terminated surfaces are characterized by high density surface states that cause Fermi level pinning.

3.4 Determination of minority carrier lifetime

The contactless C-V system also enables determination of the bulk minority carrier lifetime τ and the surface generation velocity S by the Zerbst plot analysis of capacitance transients. However, anomalous results were obtained on air-exposed free surfaces. An example is shown in Table 1 where the same wafer was measured in three consecutive states, i.e., the initial air-exposed state, then, thermally oxidized state and finally air-exposed state after removal of the thermal oxide. The drastic change of the bulk lifetime τ in Table 1 cannot be true, and indicates that strong surface recombination on free surfaces drastically affect the determination of bulk life time. This result seems to raise an important issue concerning the validity of various methods used commonly in the solar cell community to separate bulk life time and surface recombination velocity on wafers with free and passivated surfaces.

4. Conclusion

The PL method and the contactless C-V method were applied to three kinds of silicon wafers (i) air-exposed surface, (ii) hydrogen-terminated surface prepared by Higashi's method using NH_4F, and (iii) thermally oxidized surface in dry oxygen. Both PL and C-V methods gave similar surface state density distributions, and indicated presence of high densities of surface states and Fermi level pinning on air-exposed and hydrogen-terminated surfaces. From the Zerbst plot, analysis of capacitance transients on air-exposed free surfaces, a serious question was raised concerning the validity of the usually accepted method of bulk lifetime and surface recombination contributions.

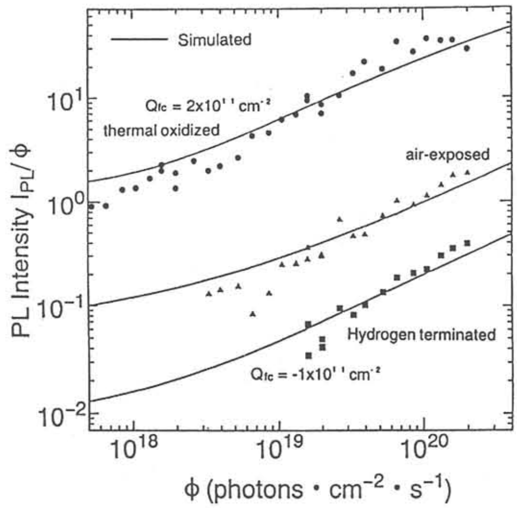

Fig.6 Measured and calculated behavior of PL efficiency

Table 1 τ and S from Zerbst plot on the same wafer

	τ (μs)	S (cm/sec)
Initial air-exposed Si	0.773 0.778	3.14 7.47
Thermal oxidized Si	423 579 550	3.18x10^{-2} 2.28x10^{-2} 2.15x10^{-2}
Air-exposed Si after removal of oxide	0.997 0.987 0.945	1.23x10^{-1} 3.76x10^{-1} 2.39x10^{-1}

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