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Tondi Electronics, Tallinn[1]) *(a) and*
Institute of Physics, Estonian Academy of Sciences, Tartu (b)

ESR Investigation of the Si–SiO_2 System

By

D. KROPMAN (a) and T. KÄRNER (b)

The defect structure of the Si–SiO_2 systems subjected to various annealing and ultrasound treatments is studied by ESR at 20 and 115 K. ESR spectra of phosphorus atoms and P_A centers are detected. The correlation between the densities of these defects in differently treated Si–SiO_2 systems is investigated. These data are found to support the model of P_A centers as vacancy complexes.

Дефектная структура системы Si–SiO_2 исследовалась методом электронного парамагнитного резонанса (ЭПР) при 20 и 115 К. В спектрах ЭПР наблюдаются линии P_A-центров и сверхтонкого взаимодействия электронов проводимости с ядрами ^{31}P со спином 1/2 атомов фосфора. Отсутствие корреляции между сигналами ЭПР от P_A-центров и сверхтон – кого взаимодействия свидетельствует о том, что P_A-центры не связаны с фосфором. Обнаружена взаимосвязь между внутренними механическими напряжениями в структурах Si–SiO_2 и P_A-центрами. Полученные результаты подтверждают вакансионную природу P_A-центров.

1. Introduction

The diminishing of the size of integrated circuit elements results in an increasing influence of point defects on their electrical parameters. The investigation of the nature of point defects in Si–SiO_2 – the basic part of an integrated circuit – is therefore of great scientific and practical interest. Among common analytical techniques electron spin resonance (ESR) has shown a substantial ability of revealing the atomic structure and position of defects in the Si–SiO_2 system. The study of the structure of MOS (metal–oxide–semiconductor) devices by means of ESR began twenty years ago [1]. A number of defects designated P_A, P_B and P_C have been discovered. In subsequent works it has been established that P_B centers are connected with the nonsaturated broken bond of silicon atoms of the Si–SiO_2 interface [2]. The nature of P_A centers is not completely understood. The absence of P_A centers in p-type silicon has allowed a suggestion that the ESR signal of P_A centers arises from donor atoms [2] or from conduction electron resonance [3]. In [4] it was established that changes in the intensity of the ESR signal of P_A centers follow an Arrhenius-type temperature dependence with the activation energy ≈ 3.5 eV, that is nearly equal to the activation energy of divacancies in silicon [4] and to the formation energy of oxygen vacancies (E′ centers) in SiO_2 [5]. This allows to suggest that the ESR signal of P_A centers is complex and is connected with vacancy complexes and oxygen vacancies at the Si–SiO_2 interface in silicon and SiO_2, respectively [6]. In this paper, we present some new experimental results in the investigation of the Si–SiO_2 system by means of ESR supporting this model of the P_A center.

[1]) Kuldnoka str. 15–64, EE-0006 Tallinn, Estonia.

2. Experimental

n-type silicon with 15 Ωcm resistivity and (111) orientation was used. The oxides were thermally grown in dry oxygen at 1100 to 1200 °C. The thickness of the oxide layers was about 0.4 μm. ESR spectra were taken at 115 and 20 K by an X-band ERS-231 spectrometer. For low-temperature measurements an Oxford Instruments helium continuous flow cryostat ESR900A was used.

At 20 K a line doublet appears in the ESR spectra due to the hyperfine interaction of an electron localized on the phosphorus atom with $I = 1/2$ nuclear spin of the ^{31}P atom [7]. It is obvious that if P_A centers are connected with conduction electrons, there must be strong correlation between the concentrations of P_A centers and the observed phosphorus centers.

It is well known that in $Si-SiO_2$ systems during their preparation there appear internal mechanical stresses (IMS). These IMS are caused by the crystallographic misfit between film and substrate and by the difference in their thermal expansion coefficients. The generation and redistribution of defects brings about a relaxation of mechanical stresses. On the other hand, IMS cause a rupture of bonds of silicon atoms and lead to the formation of point defects. This suggests a mutual dependence between the density of P_A centers and IMS. To check this assumption measurements of ESR of P_A centers and bending of identically prepared samples were carried out. The IMS and the density of point defects were varied by changing the oxidation temperature and the annealing time (from 20 to 60 min).

The density and the type of point defects in $Si-SiO_2$ systems may also be varied by ultrasonic treatment (UST) [8]. The UST of silicon samples was carried out before oxidation by means of a $LiNbO_3$ transformer at the frequency $\approx 10^2$ kHz. The amplitude of ultrasonic vibration was varied by changing the output voltage of the generator.

3. Results and Discussion

In Fig. 1 ESR spectra of a $Si-SiO_2$ sample at 115 and 20 K are shown. At 115 K the ESR spectrum consists of the signal of P_A centers with $g = 1.9996$, at 20 K there dominates the

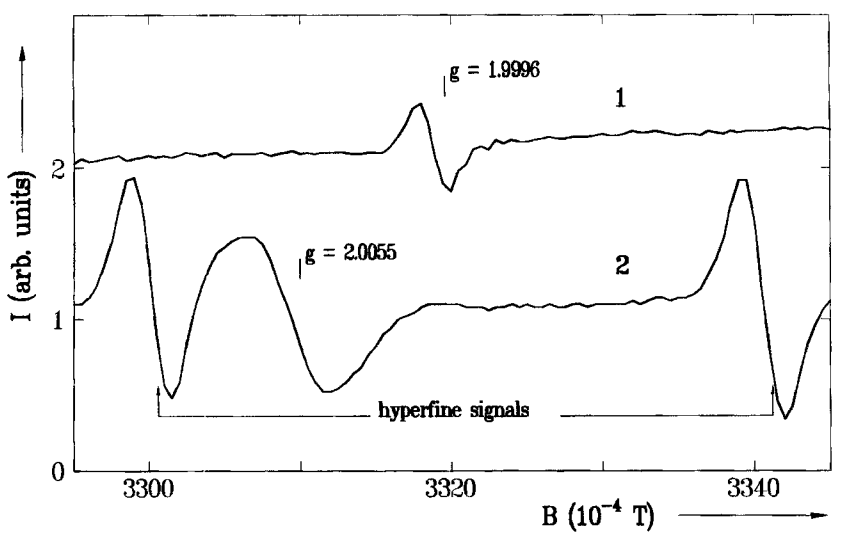

Fig. 1. ESR spectra of $Si-SiO_2$ samples at 115 K (1) and 20 K (2)

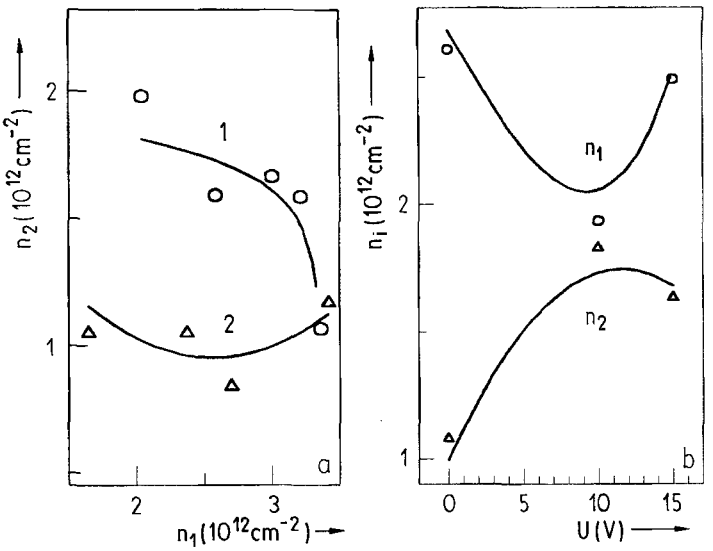

Fig. 2. a) The relation between the densities of P_A (n_1) and phosphorus (n_2) centers for Si–SiO_2 (1) and Si (2) samples and b) their dependence on the amplitude of ultrasonic vibration

signal of the phosphorus center split by hyperfine interaction. Fig. 2 depicts the densities of P_A and phosphorus centers determined by ESR for two series of specimens: Si–SiO_2 and Si, and the dependence of the density of P_A centers on the amplitude of the ultrasonic vibration for the samples having gone through a UST.

It follows from Fig. 2 that there exists no strong correlation between the concentrations of phosphorus donor centers and P_A centers. Hence, P_A centers are not connected with conduction electrons. The slight negative correlation between the numbers of P_A and phosphorus centers in Si–SiO_2 specimens can be explained by the ionization of the donor levels of phosphorus atoms or the creation of acceptor centers; the absence of a mutual dependence between the densities of P_A centers and phosphorus atoms in silicon may be due to the presence of another compensating center with higher density than the P_A center, such as broken bonds of silicon atoms ($g = 2.0023$). UST is accompanied by the creation of broken bonds in silicon and the enhancement of the ESR signal with $g = 2.0055$. The nonmonotonical variation of the ESR signal intensity of P_A and phosphorus centers with the amplitude of ultrasonic vibration may be connected with a competition between the creation of point defects and their annihilation, their antibate behavior showing that P_A centers are rather acceptors than donor centers.

In Fig. 3 the dependence between the bending of the samples and the ESR signal intensity of P_A centers for two sample series with oxides produced at 1100 and 1200 °C is shown. In case of lower oxidation temperature the bending of samples decreases with the increase of the ESR signal intensity, and at higher oxidation temperature the bending of samples and intensity of the ESR signal increase simultaneously. In the first case it may be due to the relaxation of stresses by generation and redistribution of point defects, in the second one, the creation of point defects and broken bonds of silicon atoms by the stresses. The dependence between density of P_A centers and mechanical stresses in Si–SiO_2 is an indirect evidence of the structural nature of P_A centers.

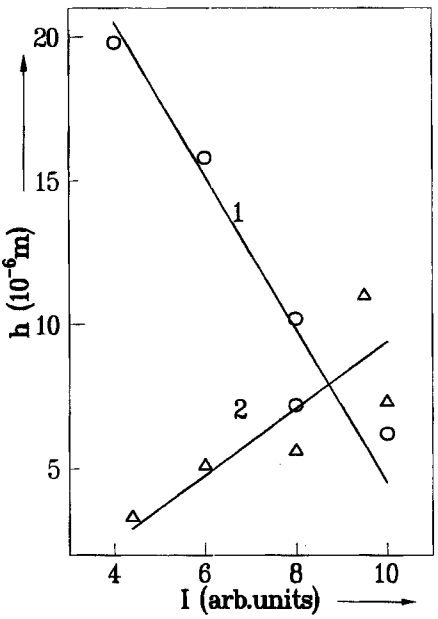

Fig. 3. The relation between the bending of samples and the ESR signal intensity of P_A centers for the samples oxidized at 1100 (1) and 1200 °C (2)

Contrary to the P_B centers whose ESR signal intensity follows the Curie law, the temperature dependence of the ESR signal of the P_A centers is more complicated. It is observed only in the temperature interval of 20 to 140 K. With increasing temperature its linewidth goes through a minimum. A similar $\Delta H(T)$ behavior was observed for the ESR signal of divacancies created in silicon by high-energy electron irradiation and it was interpreted on the basis of the Jahn-Teller effect [9]. The reorientation energies for P_A centers and divacancies determined from $\Delta H(T)$ coincide and equal ≈ 0.07 eV. The low value of the activation barrier for defect reorientation allows one to suggest that it is connected with charge transfer between different defect states. The lowering of the defect symmetry, the splitting of the degenerate levels, and the appearance of new states in the conduction (or valence) band may explain the observed increase of cavity losses in the range of temperature where the ESR signal of P_A centers appears.

The reconstruction of dangling bonds on a silicon surface and the appearance of an ESR signal with $g = 2.0043$ under powerful laser irradiation has been observed in [10]. It was suggested to be due to the Jahn-Teller effect stimulated by high-energy electron excitation of a semiconductor. In our case the reconstruction of defects, which brings about the appearance of the ESR signal of P_A centers, may be stimulated by the change of mechanical stresses during sample cooling. This is partially confirmed by the relation existing between the stresses and the ESR signal of P_A centers.

4. Conclusion

It follows from the results presented above that P_A centers created in silicon surface layers by thermal oxidation are connected with complexes of vacancies (presumably divacancies). Vacancy centers influence structural properties of the $Si-SiO_2$ interface during the process of its formation. The density of vacancy complexes may be varied by ultrasonic treatment.

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