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INVESTIGATION OF THE INFLUENCE OF OXYGEN PLASMA ON THE ELECTRICAL PROPERTIES OF Si—SiO$_2$ INTERFACE*

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Changes of the density of paramagnetic centres in the vicinity of the silicon — thermal silicon dioxide interface, effected by oxygen plasma treatment, are compared with changes in the density of effective surface states of the experimental MIS structure. A decrease of both densities was observed.

It is suggested that Si-atoms in the vicinity of Si—SiO$_2$ interface with one unsaturated bond appear in the paramagnetic spectrum.

ИССЛЕДОВАНИЕ ВЛИЯНИЯ КИСЛОРОДНОЙ ПЛАЗМЫ НА ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ГРАНИЦЫ РАЗДЕЛА Si–SiO$_2$

В работе проводится сравнение изменения плотности парамагнитных центров на границе раздела кремний – термическая двуокись кремния, вызванного обработкой в высокочастотной плазме, с изменениями плотности эффективных поверхностных состояний экспериментальной МДП-структуры. Наблюдалось понижение обеих плотностей. Предполагается, что в парамагнитном спекте сказывается влияние атомов кремния с одной ненасыщенной связью вблизи границы раздела Si—SiO$_2$.

I. INTRODUCTION

The low temperature rf discharge plasma in various gases has become a useful technological tool in manufacturing semiconductor devices and integrated circuits. The chemical reactions in plasma are employed for removing photoresist films that served as etch stops [1], [2], for the cleaning of solid surfaces [3], for the deposition of thin dielectric layers [5], [6], and for the etching of dielectric, semiconductor and metallic thin films [7], [8].

One of the basic questions to be answered before introducing this technology into microelectric devices manifacturing is the question of plasma influence on the

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** Institute of Electrical Engineering, Slov. Acad. Sci., Dúbravská cesta 4, CS — 809 32 BRATISLAVA electrical parameters of the prepared devices, mainly of those with insulator — semiconductor interfaces (MIS structures). Results of various authors [9], [10] as well as our own experiences [2] call attention to a possible generation of electric-type defects in the dielectric thin films or in the insulator — semiconductor interface region of the MIS structures, respectively.

The purpose of the paper is to investigate the oxygen plasma influence on the electrical properties of the Si—SiO$_2$ interface region. The structure silicon — silicon dioxide was studied by means of the electron spin resonance taking into consideration the results of Nishi [11], who observed three kinds of paramagnetic centres denoted as P_A, with the isotropic Landé splitting factor $g \sim 2.000$ and centres P_B with an anisotropic $g \sim 2.000$—2.010 are located in the oxide, while P_C-centres which also had an anisotropic g-value of ~ 2.06—2.07 are in silicon in the vicinity of the Si—SiO$_2$ interface.

The changes in the density of paramagnetic centres effected by the oxygen plasma treatment are compared with the changes in the density of surface states obtained by C—V measurements.

II. SPECIMEN PREPARATION

It is well known that highly conductive materials lower the quality of the ESR spectrometer cavity. Therefore, samples from high resistivity silicon were prepared. We used partially compensated p-type silicon with a resistivity of about 10.000 Ωcm. 400 μm thick Si wafers lapped and polished on both sides were thermally oxidized in an O$_2$—H$_2$ atmosphere at 1050 °C. Because of a strong sensitivity of high resistivity silicon to the temperature regime at the end of the oxidation process, the wafers were cooled from 1050 °C down to 92 °C at the cooling rate of about 80 °C/min. Post-oxidation annealing of the samples was done in an Ar atmosphere at 200 °C. The elipsometrically measured thickness of the SiO$_2$ film was found to be (620 ± 10) nm.

The wafers were cut into 2.5 mm wide and 10—20 mm long strips adjusted for the ESR spectrometer sample holder. The strips were randomly divided into 7 sets each consisting of 4—5 pieces with the total Si—SiO$_2$ interface area of the samples in one set about 3 cm^2.

The samples were treated in rf inductively coupled oxygen plasma ($f = 13.56$ MHz, ~ 100 W) operating at a pressure level of $\sim$ 26 Pa. The strips were put into a cylindrical reactor vertically to its longitudinal axis. The exposure times in the oxygen plasma were 20 s, 100 s and 180 s, respectively. The relatively short exposure times were chosen with respect to our previous experience that after 5 minutes plasma treatment the ESR spectra were not detectable at room temperature. Some plsma-not-treated samples were used for comparison.

III. EXPERIMENTAL PROCEDURE AND RESULTS

Electron spin resonance absorption was measured with the Varian A-4 spectrometer at -170°C (in order to increase resolution about 40 times compared to the room temperature measurements). The samples were inserted in a glass ampoule round which air cooled in liquid nitrogen circulated.

The spin density of each centre was esimated by comparing the measured spectra $E'' = f(H)$ and the spectra of the WEAK PITCH standard (10^{13} centers with $g = 2.001$). The spectra were measured at four different angles (0°, 30°, 60°, 90°) between H and the normal to the largest surface of samples. The field modulation frequency was $f_m = (9.120 \pm 5)$ MHz. The mean magnetic field was $H_{aver} = (3.200 \pm 2)$ Oe.

The Zaininger method was ussed in order to determine the density of effective interface states in the Si—SiO$_2$ structure. Since no tabulated values of parameters needed for the calculation of effective interface states density are available for high resistivity silicon substrates, extrapolation was used.

Circular contacts were prepared by evaporating Al on the oxidized silicon surface, the lower-surface large-area contact was made by rubbing in galium by means of corundum powder and an Al rod. The measuring signal with a frequency $f_m = 1.592$ kHz and an amplitude 30 mV was employed. The saw-tooth voltage was changed at the rate of 0.3 V/s. Some of the measured C—V curves had not a high frequency character. We ascribe this to inhomogeneity of high resistivity silicon. No futher evaluation was attempted.

Contrary to [11] only two types of paramagnetic centres were observed by radiospectroscopy. The density of A-centres was found to be $E_A \sim 10^8$ — 3.5×10^9 spin/cm^2 with the g-factor being 2.000. The obtained density of B-centres was $E_B \sim 4.8 \times 10^9$ — 2.9×10^{10} spins/cm^2 with the g-factor of 2.007 with no observable anisotropy within the accuracy of measurement ($g = 2.007 \pm \pm 0.002$).

Although the value of density is calculated within 30 % to 50 % error limits we may conclude that number of paramagnetic centres in the MIS structure decreases proportionally with the time of treatment in oxygen plasma (Fig. 1).

The shape of many measured C—V curves do not allow an unambiguous determination of the conductivity type in the measured location of the silicon substrate. If the original (i. e. p-type) conductivity is preserved, then the density of effective surface states N_{ss} (as well as the flat band voltage V_{FB}) slowly decreases with time as samples are kept in oxygen plasma. Independently of the conductivity type of the substrate a longer stay of the samples in oxygen plasma causes a narrower non-linear capacity region in the studied MIS structures. The measured density of effective surface states N_{ss} ranged from 2.7×10^{11} to 4.4×10^{11} cm^{-2} (in the p-type substrate).

Although the measured values indicate some correspondence between E and N_{ss} it does not suffice to confirm any correlation between the densities of paramagnetic centres and effective surface states on the basis of the obtained results. The drops of N_{SS} and E_B (E_A) may be related with a prolonged stay of the samples in plasma. It is more probable that there is a connection with B-centres since their density is by one order higher. Nishi considers these centres as unsaturated Si-bonds in a Si—O network. According to [13] these silicon ions form a fixed defect charge Q_F in the vicinity of the Si—SiO$_2$ interface, contributing to the effective surface charge eN_{SS} thus influencing V_{FB}. Obviously, such defects behave as electron traps, i.e. at a positive gate voltage on the MIS structure the charge Q_F should be partially neutralized by electrons that are able to tunnel into these traps. Thus it seems that in the paramagnetic spectra only free traps (Si atoms with one unsaturated bond) appear in the vicinity of the Si—SiO$_2$ interface. Since the value of E_B is by one order lower than N_{SS}, the change of E_B is only a partial contribution to the decrease of N_{SS} after plasma treatment.

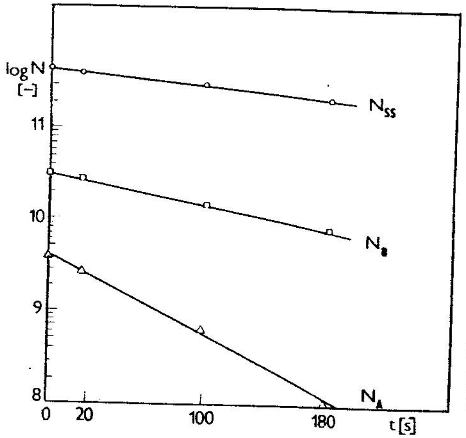

Fig. 1. Effective surface states density (N_{ss}) and paramagnetic centers density (N_A, N_B) as functions of the treatment time of Si—SiO$_2$ structures in HF oxygen plasma.

IV. CONCLUSION

The aim of this paper was to investigate the influence of oxygen plasma on the electrical properties of the Si—SiO$_2$ structure. Our experiments yields the following unambiduous conclusions: 1) There are two types of paramagnetic centres (A and B, c.f. [11]) occuring in the investigated Si—SiO$_2$ structures. 2) The density of the centres is of the order 10^9 to 10^{10} spins cm^{-2}. 3) Applied oxygen plasma decreases the density of paramagnetic centres. 4) In oxygen plasma the density of the effective surface states decreases.

Our measurements indicates a connection between the densities of paramagnetic centres and effective surface states. It is possible that Si-atoms in the vicinity of Si—SiO$_2$ interface with one unsaturated bond appear in the paramagnetic spectrum.

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