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Synthesis of charged silica films of porous structure

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A new technique has been proposed to obtain thin charged dielectric silica films with porous structure on a Si surface. The film composition and charge state of the dielectric/semiconductor system obtained have been studied. Thickness and porosity degree of the synthesized films have been estimated. The films have been shown to be similar in structure to silica aerogel. The films using in the semiconductor microelectronics, in particular, for sensors and solar cells is proposed.

Предложен новый метод синтеза тонких заряженных диэлектрических пленок кремнезема с пористой структурой на поверхности кремния. Исследован состав пленок и зарядовое состояние полученной системы диэлектрик-полупроводник. Сделаны оценки толщины и степени пористости синтезированных пленок. Показано, что структура пленок приближена к структуре аэрогеля кремнезема. Предложено применение таких пленок в полупроводниковой микроэлектронике, в частности, для создания солнечных элементов и сенсоров.

The $Si–SiO_2$ structures are being used widely for a long time in the microelectronic technologies. The technique proposed in this work for silica film synthesis makes it possible, in contrast to traditional oxidation technique [1], to obtain porous charged films with the structure similar to silica aerogel which, due to its outstanding thermal and electric insulation properties, low density, and high porosity, might belong to promising materials for modern technologies [2–4]. In contrast to the existing techniques of aerogel synthesis [2–4], the Si substrate material is used for formation of the films, thus, a dielectric-semiconductor system typical of microelectronic structures is directly synthesized. To provide conditions suitable for formation of the porous silica films, Si is oxidized in aqueous solution of KOH or NaOH, thus favoring formation of siloxane bonds of the gel spatial structure under rotation of the Si wafer.

The on-silicon porous dielectric silica films were synthesized on monocrystalline boron doped Si wafers with electric conductivity of 10 Ohm·cm. The wafer surface coincided with the crystallographic plane (100). The wafers were chemically treated using a standard procedure usually employed prior to thermal oxidation [1]. Thereafter, the wafers had been placed on a centrifuge stage and rotated at 3000 to 3500 rpm. KOH solution of (10^{-5}–10^{0}) M concentration was supplied to the wafer surface by means of a dosing unit. The formed films possess a bilayer structure. The upper layer of residual KOH and potassium silicate formed in the course of the reaction was removed by washing with deionized water. No compounds or impurities untypical of $Si–SiO_2$ system have been found in the films by Auger spectrometry and laser mass-spectroscopy. The film impedance was measured by putting an indium probe in the contact with the film surface and applying both a constant voltage and RF testing signal. The obtained dependences were typical of the RF C-V curves specific for the metal-semicon-

ductor structures. This evidenced dielectric nature of the formed films. The breakdown voltage depends on concentration of the alkali solution.

The charge state of the dielectric/semiconductor structure was studied using the dynamic capacitor technique [5–7]. In these investigations, voltage V_k is measured that appears between the vibrating probe electrode and the semiconductor wafer. A variable voltage $V_k \neq 0$ between the electrodes of the dynamic capacitor arises if a thermoelectric work function difference exists between the probe electrode material, on the one hand, and the semiconductor, on the other one. One more reason for appearance of this voltage is the presence of charge Q_d inserted inside the dielectric film covering the semiconductor material. The V_k voltage was measured both in dark and under illumination, thus allowing us to separate the contributions to V_k from charges located in the dielectric and in the semiconductor. In the spot of measurement, the sample was illuminated with laser light of $\lambda = 0.63$ μm wavelength and 5 mW power. The V_k measurement was performed in 200 points on a surface of each of the plates with subsequent averaging of the obtained results. Dispersion of the measured values constituted 5 or 10 % for both within a single wafer and within each 4-wafer stack. It should be noted that the described experiments and investigations were also accomplished with using NaOH solution. Their results are similar to those obtained with KOH.

Typical results of V_k voltage measurements as a function of concentration M of the solution used to prepare the film are presented in Fig. 1. In the dark conditions, $V_k = V_{kd}$ with V_{kd} being a value that characterizes the charge state of the system in the equilibrium (curve *1*). Under intense illumination of the sample, energy zones of the semiconductor surface layer become straightened, and conductivity of this layer approximates to that of a metal. In this case, $V_k = V_{kl}$ (with V_{kl} being a voltage measured between the probe electrode and the silicon), provided that both the near-surface bending of the energy zones φ_s and width l of the spatial charge area are equal to zero (curve *2*). Curve *3*, Fig. 1, calculated by formula $V_{kf} = V_{kd} - V_{kl}$ is equal to φ_s. Under illumination, $\varphi_s \approx 0$, and values $V_k = V_{kf}$ given by curve *3* are values of the surface photoelectric electromotive force.

In curves $V_k(M)$, Fig. 1, two pronounced sections are observed. The first one is a plateau within the interval of $(0–10^{-4})$ M. In this interval, equation $V_{kf}(M) = V_{kd} - V_{kl} \approx 0$ (curve *3*) is valid and, hence, the zone bending is $\varphi_s \approx 0$. Within the second section, for $M > 10^{-3}$, the V_{kd} and V_{kl} values start to trend towards negative values, and absolute value of $V_{kf}(M) = V_{kd} - V_{kl}$ starts to rise sharply. This is an evidence of the sharp rise of φ_s (downward bending of the zones), which is possible only if the Q_d charge, inserted into the dielectric film, gets increased. Its value begins to prevail over the surface state charge located at the film/semiconductor interface, with the charge sign being positive. Therefore, the $V_k(M)$ curves in Fig. 1 represent variations of Q_d charge with increase of the solution concentration M. Such a behavior is caused by insertion of K^+ ions into the film's bulk in the course of its formation in the KOH solution. The curves $V_{kd}(M)$ and $V_{kl}(M)$ shown some variation in their arrangement relative to the ordinate axis for different wafer stacks. This was due to uncontrolled variations of the boron dopant content in Si. This gives a small change in the curve shape, and their origin at $M = 0$ falls into the region of $V_k = \pm 0.2$ V.

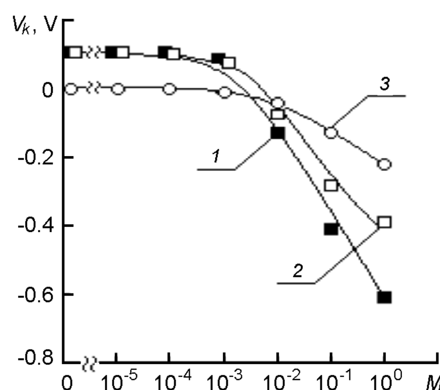

Fig. 1. Dependences of $V_k(M)$. Curves *1* and *2* correspond to $V_k = V_{kd}$ and $V_k = V_{kl}$, respectively. Curve *3* corresponds to $V_{kf} = V_{kd} - V_{kl}$.

Curve *1* in Fig. 2 shows data obtained when measuring the film thickness by ellipsometer. Since the film permittivity was unknown, the value $\varepsilon = 4$ was taken when measuring d, which characterizes the thermally grown SiO_2. When comparing curve *1*, Fig. 2, and curve *1*, Fig. 1 it is seen that both the film thickness and the charge therein increase as functions of M according to an approximately the same law. Supposing the K^+ ion distribution across the film thickness to be homogeneous, we can

estimate the film thickness basing on experimental data obtained from the vibrating capacitor measurements. With V_{kl} and $V_{kf} = V_{kd} - V_{kl} \approx \varphi_s$ being known, we can calculate capacity C_{sc} and charge Q_{sc} of the space-charge region [8]. Neglecting the surface state charge in comparison with that inserted in the film, we take $Q_{sc} \approx Q_d$ and estimate the dielectric film thickness using the plane capacitor formula with taking into account that Q_d charge is distributed homogeneously across the film thickness. The silica grating constant was taken as a minimal distance between the K^+ ions and the film/silicon interface.

The $d(M)$ calculation result is presented by curve *2* in Fig. 2. At the section of $(10^{-4}-10^{0})$ M, this dependence is described approximately by empiric formula $d = k\lg M$ with k being proportionality coefficient. From comparison of the curves *1* and *2* it is seen that d value obtained from the $V_k(M)$ measurements is 3 to 6 times larger than that obtained from the ellipsometric measurements for the same ε values. Since the plane-capacitor calculations of the film thickness give $d \sim \varepsilon$, and the ellipsometric measurements give $d \sim 1/(\varepsilon - \sin^2\varphi)^{1/2}$, then such a difference can be explained only by the film porosity and by a difference between the permittivity effective value ε_{eff} and the value taken for the calculation. By adjustment of the ε value, one can achieve an approximate coincidence of the $d(M)$ dependences, Fig. 2, within the investigated section of M concentration, when taking $\varepsilon_{eff} \approx 1.5$. In the presence of pores, the effective permittivity ε_{eff} of a porous material can be determined using the Lichtenecker formula for two-component dielectrics. If the electric field is directed normally relative to the pores orientation, then $1/\varepsilon_{eff} = (1-\alpha)/\varepsilon_1 + \alpha/\varepsilon_2$ with a being volume concentration of the pores, and ε_1 and ε_2 are permittivities of the solid material and the pores, respectively. When taking $\varepsilon_2 = 1$ (air-filled pores) and $\varepsilon_2 = 4$, we obtain $\alpha \approx 0,5$. All the above-stated allows us to conclude that structure of the investigated films is of porous type.

The epitaxial destructive growth [9] is the most probable mechanism of the porous silica film formation on a silicon wafer surface. Silica and its hydrated molecules needed for synthesis of the wet gel are formed in the course of the known reaction between silicon and water. Structure of the

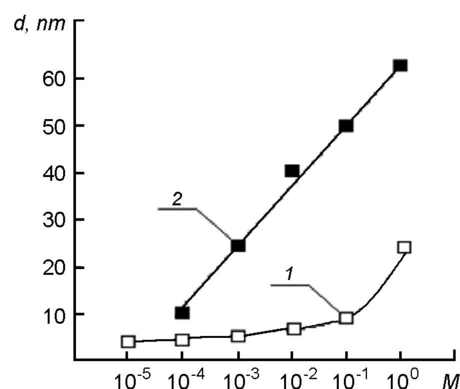

Fig. 2. Dependences of silica film thickness d on solution concentration M. Curve *1* is measured by ellipsometer and curve *2* is calculated from data of Fig. 2.

formed gel and its porosity degree are determined by the elementary island tetrahedrons $[SiO_4]^{4-}$ and their complex spatial formations. The gel structure also depends on the energy state of the silicon surface, its composition, and conditions of the reaction. The porous structure of the film formed due to the mycelia colloidal solution polymerization, similar to reactions which are used for silica aerogel synthesis. The porosity degree of the synthesized films ($\alpha \approx 0,5$) is close to the data of references [2–4]. Together, this permits us to conclude that structure of the investigated films is similar to silica aerogel structure.

The studied novel technique for on-silicon formation of porous silica films enables to form dielectric films with a needed amount of the inserted charge at room-temperature. Such films may be employed in insulation components of microelectronic devices and for passivation of silicon surface. The features of porosity and presence of the embedded charge provide additional possibilities. The charge inside the dielectric film enables formation of a inverse bending of the energy zones on a semiconductor surface and surface-barrier solar cells [10].

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Синтез заряджених плівок кремнезему з пористою структурою

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Запропоновано новий метод синтезу тонких заряджених діелектричних плівок кремнезему з пористою структурою на поверхні кремнію. Досліджено склад плівок і зарядовий стан отриманої системи діелектрик-напівпровідник. Зроблено оцінки товщини і ступеня пористості синтезованих плівок. Показано, що структура плівок є близькою до структури аерогелю кремнезему. Запропоновано застосування таких плівок у напівпровідниковій мікроелектроніці, зокрема при створенні сонячних елементів і сенсорів.