SILICON NANOCLUSTER IN SILICON DIOXIDE

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Cathodoluminescence spectra of silicate systems, have two well-known bands associated with native SiO_2 defects, namely, a red one peaking at 1.9 eV (twofold-coordinated silicon). The position and intensity of these bands in thermally grown films vary depending on the silicon type and the technology of the film preparation. The bands are the strongest for films grown on *p* silicon. A layer - by - layer analysis of thermal oxide films on *p* silicon showed that the band in green spectral region appears on the interface and on the adjoining oxide layers 0.1-0.2 um thick. To establish the nature of the centers responsible for the green bands, we studied cathodoluminescence spectra of various silicate systems

In order compare the experimental spectra and determine the position of the maxima of the broad bands with a higher accuracy, the spectra obtained were deconvolved into their constituents. This deconvolution was made using the ORIGIN 6.0 code. This was done under the assumption that the band shape can be fitted by Gaussians. The thin lines in the figures presented in this paper show the results of the deconvolution. Similar cathodoluminescence spectra in the green region (2.1 - 2.2 eV) appear in various silicate matrices as the excitation density increases. In /1/ this band is assigned to silicon nanoclusters. High excitation densities produce free silicon atoms in the bulk of the silicate matrix, which may form nanoclusters. The size of the nanoclusters is determined by that of the voids in the sample.

These considerations underlie the choice for further study of a sample with known dimensions of its voids, namely, opal. Opals are regularly arranged arrays of silicon oxide spheres 200 — 250 nm in diameter. Opals have voids measuring 5, 10, and 15 nm. As the excitation density is increased, small nanoclusters form, which subsequently fill the smallest (5 nm) pores.(Fig 1) The TEM studies reveal that, on the surface of SiO_2 spheres 250 nm in diameter, there are silicon nanoclusters 4 to 5 nm in size.

The samples were prepared from (100)-oriented *p*-type, 10 Omsm silicon single crystal (c-Si) plates. The oxide film containing silicon nanoclusters was formed using the following procedure. A c-Si plate was electrochemicaly etched in an aqueous solution of hydrofluoric acid (30

% HF) for 5 min at a current density of 10 *mA/cm2,* which resulted in a porous silicon (por-Si) layer formation.

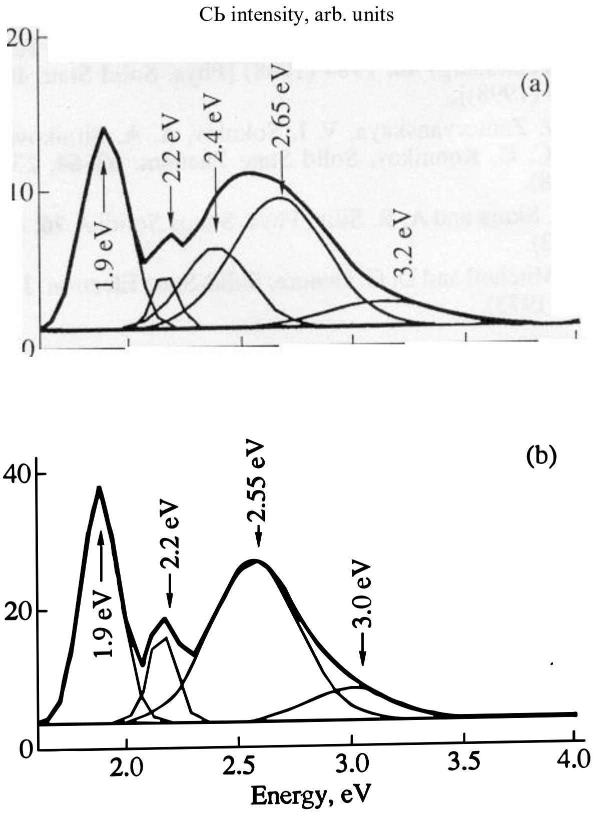

Fig.1 CL spectra of the opal obtained under various excitation conditions. Voltage (kV), current (nA), and exposure time (ms): (a) 10, 1.5, and 100; and (b) 10, 1.5, and 300, respectively.

A part of the plate remained unetched to serve as a control region in subsequent measurements. After etching, the material was oxidized by exposure to water vapor at 1000'C for 20 min. The oxide film thickness in the control (c-Si) region was 190 nm, while that on por-Si was 300 nm. The conditions of oxidation were specially selected so that the entire por-Si layer would be oxidized together with some part of the underlying single crystal substrate material.

The presence of such nanoclusters in our samples was detected by measuring their cathodoluminescence spectra (Fig 2).

The current-voltage (I-U) characteristics of MOS structures were measured in the dark, in a dynamic regime using a sinusoidal probing signal at a frequency of 20 or 400 Hz. The measurements were performed under standard conditions in a vacuum chamber, which eliminated the influence of adsorption. In order to expand the range of conditions studied, the I-U curves were measured at two significantly different temperatures, 300 and 77 K (the quantum size effects are most probably manifested at lower temperatures).

The I-U characteristics of all samples with oxidized porous films (Figs. 3 and 4) exhibited the following common features (for the convenience of analysis and comparison with other published data, the I-U curves are plotted on a linear scale):

(i), all I-U curves are nonlinear, which is evidence of the diode effect;

(ii) in all I-U curves, the current at a zero bias voltage has a finite nonzero value;

(iii) the I-U curves of all samples exhibit hysteresis.

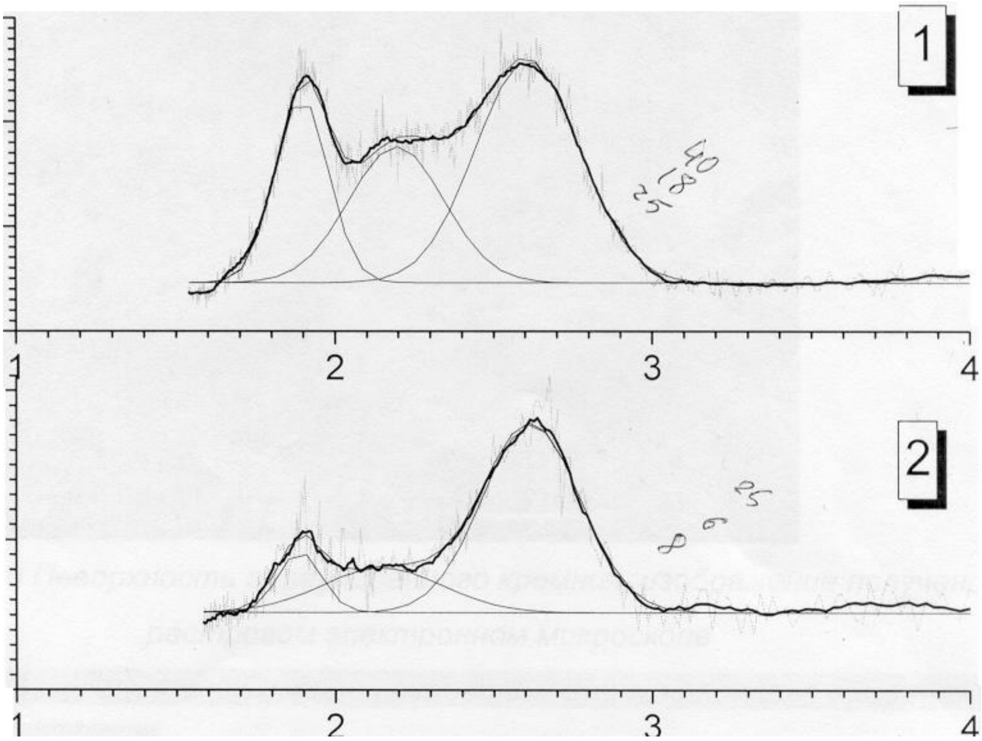

Fig.2. CL spectra of oxided silicon 1 - por-Si 2 -c-Si

At the same time, the control samples exhibited neither diode properties nor a finite zero-bias current and hysteresis. The hysteresis behavior, as well as a plateau on the I-U curves (Fig. 3) seem to reflect the accumulation of charge at the interface in biased samples with minus on c-Si, which is due to nc- Si grains possessing the properties of slow traps. The charge carrier trapping is determined by the amplitude of the measuring signal, which is confirmed by the fact that a short (12 **s)** "field treatment" (whereby a higher bias voltage amplitude 40 V instead of the initial 12 V, is used during this period) leads to extension of the plateau on the I-U curve (as indicated by the dashed curve in Fig. 4).

Another important feature of the I-U curves of the samples studied is the presence of a packet of high-frequency oscillations on one of the branches. The amplitude of these oscillations with respect to current probably reflects some internal properties of the MOS structure, which is differently modified during the "field treatment" and during measurement at various frequencies of the measuring signal. Figures 3 and 4 show cur- rent oscillations of different types observed on the I-U curves. Figure 3 illustrates the oscillations appearing on the plateau in the region of positive bias (plus on c-Si). Most of the samples studied showed I-U curves close to that presented in Fig. 3.

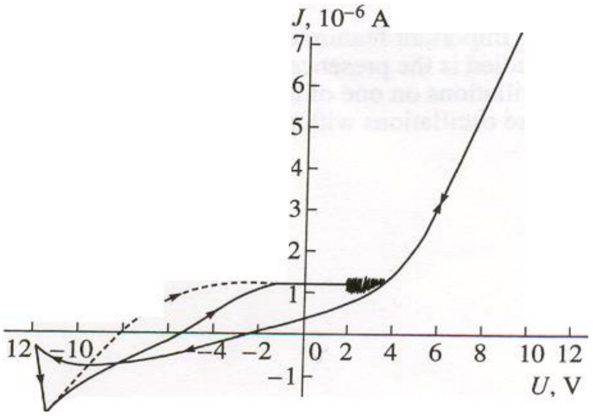

Fig..3 A room temperature I-U characteristic measured at 20 Hz), showing oscillations on the plateau at a positive polarity of c-Si substrate. Dashed curve shows the plateau extended upon the field treatment."

Figure 4 presents a I-U curve of another kind, which may be called "atypical." This curve was obtained at liquid nitrogen temperature for a sample kept for two months in a vacuum chamber. Here, the oscillations are observed on the branch corresponding to minus on c-Si. As can be seen, the level of currents measured in this case dropped sharply as compared to that at 300 K and revealed oscillations not detected at room temperature. The amplitude of oscillations in Figs. 3 and 4 is virtually the same. In all cases, the oscillations were observed only at 20 Hz and disappeared at 400 Hz. It should be emphasized that an increase in the frequency, as well as exposure to white light, eliminated the fine structure of the I - U characteristics.

The observed peculiarities of the I-U characteristics are probably indicative of the presence of shallow quantum wells in MOS structures based on oxidized porous silicon. These quantum wells are structurally related to the aforementioned slow traps. This is evidenced by the result presented in Fig. 4, where the current oscillations are observed immediately on the plateau.

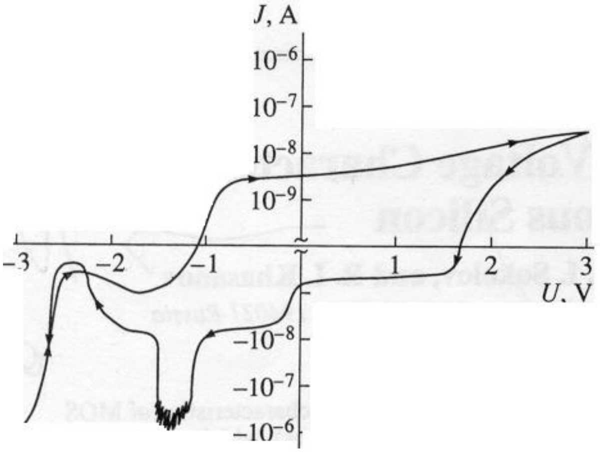

Fig.4 A low-temperature (77 K)I-U character istic of sample (kept for two months in a vacuum chamber) measured at 20 Hz), showing oscillations on the plateau at a negative polarity of c-Si substrate. No such oscillations were observed for this sample at 300 K and before keeping in vacuum.

REFERENCES

1. V.G. Baru, M.I. Elinson, V.A. Zhitov, et al., Mikroelektronika 27 (1), 45 (1998)